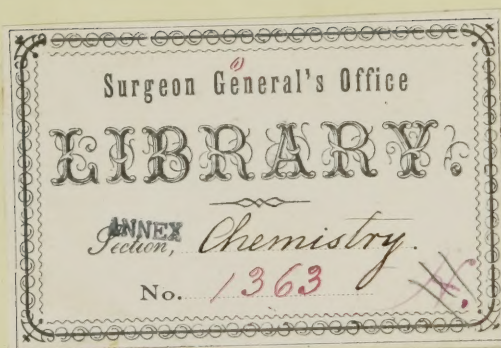




George A Otis M. D.

1853.









PRINCIPLES  
OF  
ORGANIC AND PHYSIOLOGICAL  
CHEMISTRY.

PHILOSOPHY

ORGANIC AND PHYSIOLOGICAL

CHEMISTRY

PRINCIPLES  
OF  
ORGANIC AND PHYSIOLOGICAL  
CHEMISTRY.

BY  
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TRANSLATED BY  
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PHILADELPHIA:  
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TO

JOHN WILLIAM DRAPER, M.D.,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF NEW YORK,

THIS TRANSLATION

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## ADVERTISEMENT.

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THIS work is intended as a text-book for Professors and their classes, and also for private students who wish to study the fundamental principles of Organic Chemistry. It contains not only all the older facts, but also the new discoveries, relating to the products of both the animal and the vegetable kingdom. It presents concisely the profoundest philosophy of chemistry, and may be regarded as an introduction to the author's large work. The writer's design, in its preparation, may be imperfectly understood by the following extract from his preface.

"It is constantly becoming more apparent, that the organic compounds, if all their relations are brought into view, and not alone their individual characteristics, belong to distinct groups, which, as it were, correspond to the natural families of plants, and that these groups are again united to each other by a common bond. Scientific Organic Chemistry must determine these groups, show the laws to which their members are subject, trace out the bond which unites them, ascertain from their constitution the cause of their mutual and anomalous relations, and unfold the *Oneness* in the great mass of materials. In completing these *Principles*, I have wished to contribute something to the solution of this problem, and whilst I have sought to point out, in the above-mentioned direction, the department of our knowledge in organic chemistry, in a concise scientific form, yet my especial endeavor has been to obtain a fixed stopping-point, which might make it possible for the student to review the details, and be able to impress them upon the memory."





## TRANSLATOR'S PREFACE.

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THE great extent to which Organic Chemistry is cultivated in Germany, and the increasing demand for a knowledge of that science, both in England and America, are sufficient reasons for endeavoring to conduct some of the German fountains of chemical science to our own land.

In selecting the present work for translation, regard has been had to the fact, that without being too voluminous for general use, it embraces most of the Philosophy of Chemistry, and the new discoveries not already incorporated into the systematic works in our language. This volume, as the author in his Preface remarks, is intended as an introduction to his large work, the "*Chemie der Organischen Verbindungen*," (an octavo of 3000 pages, which has long been a standard work throughout Germany, and is now being revised by the author;) yet it is complete in itself, and contains, in a clear, concise form, nearly all that is known of organic chemistry. It has been prepared expressly for laboratories, medical and scientific schools, universities, etc., and the study of a few pages will satisfy the scientific chemist that the distinguished author has well comprehended both the subject itself and the wants of the student.

In nomenclature, the translator has endeavored to use those terms which would best express to the English reader the German idea, without attempting improvements; yet he has found great difficulty, not only from the want of agreement between our present English authorities, but also from the absence of terms corresponding to the German. Where it has been necessary to use new terms, those of the author have been almost invariably retained.

As a large portion of the work was translated in Zürich,

whilst the translator enjoyed constant personal intercourse with Dr. Löwig, it is hoped that the translation does justice to the author, though, from the difficulty of the subject, it cannot be free from errors. The style, being concise, has almost necessarily lost its elegance, as no freedom in phraseology could be taken and express the exact idea. The translation of a purely scientific work like this is attended by many difficulties, not the least of which arises from the very necessity of its being rendered into English—I mean, the absence of anything of a like nature in our language; and the necessity of a right apprehension of a thousand abstruse truths, in order to their correct translation. The appreciation of these difficulties has made the translator more attentive to correctness of idea, than to any ornaments of style.

It is scarcely necessary to say that, in this work, degrees of temperature invariably refer to the centigrade thermometer.

Should this volume meet with sufficient success to justify the undertaking, and show that our chemical public are ready for such a work, it is proposed to offer to them Dr. Löwig's "*Chemie der Organischen Verbindungen*" (Chemistry of the Organic Combinations) in an English dress, as speedily as possible after the appearance of the third German edition.

DANIEL BREED.

UNITED STATES PATENT OFFICE,  
*Washington, D. C.*, 1853.

## PREFACE.

---

SINCE the appearance of my "Chemistry of Organic Combinations," the number of chemical facts has greatly increased, yet none of these has determined me to materially change the system which I there adopted; on the contrary, the new discoveries have only served to confirm it. Indeed, many views, which I there ventured only with diffidence to advance, have been so surprisingly confirmed that I no longer hesitate to use that system as the foundation of the present work. It is constantly becoming more apparent that the organic compounds, if all their relations are brought into view, and not alone their individual characteristics, belong to distinct groups, which, as it were, correspond to the natural families of plants, and that these groups are again united to each other by a common bond. Scientific organic chemistry must determine these groups, show the laws to which their members are subject, trace out the bond which unites them, ascertain from their constitution the cause of their mutual and anomalous relations, and unfold the *oneness* in the great mass of materials. In completing this volume, I have wished to contribute something to the solution of this problem; and whilst I have sought to point out, in the above-mentioned direction, the department of our knowledge in organic chemistry, in a concise scientific form, yet my especial endeavor has been to obtain a fixed stopping-point, which might make it possible to the student to review the details and be able to impress them upon the memory. In this work, as in the "Chemistry of Organic Combinations," the theory of the organic radicals forms the basis of the systems. I have gone only one step further, in considering the radicals no longer as a collective whole; for I distinguish in them an active compound-controlling part from some more passive com-

ponents. By this means it was possible, with fewer elementary substances, to combine not only a great part of the organic compounds, in a manner at once simple and corresponding to facts, but also to discover a cause for the different chemical relations of the radicals. For example, there were the phenomena of substitution, i. e. the entrance of hydrogen through the *halogens*, which I sought to harmonize with the theory of the organic radicals; by this, and without my wishing or seeking it, to a certain degree a union between the radical theory and the nucleus theory was revealed. The principles which have led me thus far, I have expressed in the General Part; very briefly, indeed, yet I trust so plainly that no one will be in doubt as to my real meaning; to prevent misunderstanding, however, I am induced to make a few further remarks.

The only object of chemical symbols is, to express through the formula the mode of union of the elements, corresponding to the reactions which have been observed in the mutual influence of the chemical combinations. Those formulæ which most nearly fulfil these conditions must be considered as the best. How the elements in a chemical compound really do unite with one another—in what the act of chemical combination really consists, whereby the entire change of qualities of the elements in their union is controlled, are questions to which a positive answer can never be given. It is alone what is chemically created—chemically completed—that is subject to our observation. The *how* of these creations, in inorganic as well as in organic nature, is entirely concealed from our view; and, in this respect, all microscopic investigations have brought nothing to light. Therefore, also, the question regarding *atoms* is immaterial; the fact is, the chemical union of substances takes place in certain atomic proportions, and the word *atom* is nothing more than an expression of this fact.

By denoting acetic acid  $(C_4H_3)O_3$ , it must be assumed that  $C_4H_3$  unite as a whole with  $O_3$ ; this formula corresponds to all the known reactions, since  $O_3$  can be substituted by  $Cl_3, Br_3, S_3$ , etc. The same is true of the formulæ  $(C_4H_5)O, (C_4H_5)S, (C_4H_5)Cl$ , etc.; and we place O, S, Cl, outside of the brackets, as the elements which are able, mutually, to substitute each other. These formulæ, in certain respects purely empirical, do not affect the ques-



tion *how* the elements in  $C_4H_3$  and in  $C_4H_5$  possibly unite, first with each other, and then with O, S, Cl, etc.

The organic compounds, like the inorganic, separate into groups, whose individual members are distinguished by common characteristics; but whilst the difference of chloric, bromic, and iodic acid from potassa, soda, and lithia, is caused by the different quality of the elements, the variations in character of formic, acetic, and propionic acid from wood-spirit, alcohol, and amyl-spirit, depends upon the difference in quantity of the same elements, and all new investigations have led to the same results—that this increase of weight is consequent upon a simple law, and in a great number of organic compounds, consists in a plus or minus  $x C_2H_2$ . If from ethyl  $C_4H_5$ , the group  $C_2H_2$  be withdrawn, there remains methyl  $C_2H_3$  and methyl— $C_2H_2$ , is  $=H$ . Now all radicals which belong to this class, and which I have designated as the radicals of the methyl group, in all their combinations, act the part of hydrogen; like it, they unite with O, S, Cl, Br, etc., and their compounds correspond, especially with N, P, As, St, in each relation of the hydrogen compounds, to those elements. Hence the character of these radicals depends upon the hydrogen atom; it controls the combinings of the whole group; in it lies the cause of their chemical commonality, whilst the individual members, and their varying relations, are determined by  $x C_2H_2$ . Hence, I designate II as the active part of these radicals, and  $x C_2H_2$  as their components. In like manner, the radicals of the groups of acids, to which acetic acid, butyric acid, etc., belong, divide into the active part  $C_2H$ , and the components  $x C_2H_2$ ; the chemical distinction between the radicals of the methyl group and those of the individual members of the above-mentioned acids, which I have generally called the radicals of the formyl group, rests therefore upon the chemical difference of the active parts.

Like ethyl  $C_4H_5$ , benzid  $C_{12}H_5$  is a member of a series in which each successive member is formed by the entrance of  $C_2H_2$ . In chemical relation, benzid behaves like ethyl; hence it is consistent to seek the cause of this agreement only in the common active part, therefore, in the hydrogen atoms; thus hydro-ethyl ( $C_4H_5$ )H corresponds to hydro-benzid ( $C_{12}H_5$ )H. Now benzid  $C_{12}H_5$ —ethyl  $C_4H_5 = C_8$ . If we consider the remainder  $C_8$  as the nucleus, benzid may be regarded as consisting of the components  $2 C_2H_2$ ,

the nucleus  $C_8$ , and the active part H. The formula for benzid is, therefore,  $2C_2H_2, C_8, H$ , corresponding to ethyl  $2C_2H_2, H$ . As benzid relates to ethyl, benzoic acid relates to propionic acid, toluyllic acid to butyric acid, and cuminic acid to capronic acid; thus is:—

Propionic acid . .  $(2C_2H_2, C_2H)O_3 + C_8 =$

Benzoic acid  $(2C_2H_2, C_8, C_2H)O_3.$

Butyric acid . . .  $(3C_2H_2, C_2H)O_3 + C_8 =$

Toluylic acid  $(3C_2H_2, C_8, C_2H)O_3.$

Capronic acid . .  $(5C_2H_2, C_2H)O_3 + C_8 =$

Cuminic acid  $(5C_2H_2, C_8, C_2H)O_3.$

These formulæ are intended only to assist the memory. How this nucleus  $C_8$  occurs in the combination, and whether it generally exists only as such, are not determinate questions, but the fact is that, by the addition of  $C_2, C_4, C_6, C_8$ , to the radicals of the formyl and methyl group, each one of the hydro-polycarblys is formed. Benzid  $2C_2H_2, C_8, H$  is related to the radical of benzoic acid  $2C_2H_2, C_8, C_2H$ , as ethyl  $2C_2H_2, H$  is to the radical of propionic acid  $2C_2H_2, H, C_2H$ .

Benzoic acid and salicylous acid belong to the most interesting isomeric compounds. With the same atomic constitution ( $C_{14}H_5O_3$ ), they show chemically and physically the greatest differences. Benzoic acid is one of the most permanent organic substances, not alone because of its expelling salicylous acid from its combinations, but, in its alkaline solution exposed to the air, it does not suffer the least change, whilst salicylous acid, under the same circumstances, soon separates into acetic and melanic acid. The cause of this different behavior can be sought only in the different mode of union of the elements. Hence, when I denote benzoic acid as  $(2C_2H_2, C_8, C_2H)O_3$ , and salicylous acid as  $C_4H_2O_2 \cdot (C_2H_2, C_6, C_2H)O$ , I wish by this to express that the former consists of *one* group of atoms, the latter of *two* separate groups. The decomposition of salicylous acid depends first of all upon the separation of these groups; and whilst one, by the addition of the elements of one atom of water, is converted into acetic acid, the other  $C_2H_2, C_6, C_2H$ , under similar conditions, forms melanic acid. In making the formulæ, I have always had these circumstances in

view; they are no *fictions*, but the result of *accurate examinations* of all the *phenomena* which the compounds present.

In the present state of Organic Chemistry, I do not think it worth the trouble to combat the objections occasionally made to the theory of organic radicals. From the fact that nitrate of silver does not react upon chlorethyl, some have at once concluded that chlorine does not occur in that substance as in chloride of potassium; and from the circumstance that, by shaking an aqueous solution of potassa with acetate of ethyl, acetate of potassa is not instantaneously formed, they find incontestable evidence that acetic acid cannot be contained as such in the compound. Yet no chemist doubts the similarity of constitution of chlorethyl and iodethyl, for it is a fact, that, by the action of chlorine upon iodethyl, chlor-ethyl is formed, whilst iodine is separated; and, in the same manner, nitrate of silver and iodethyl, in alcoholic solution, are at once transposed into iodide of silver and nitrate of ethyl. Although acetate of ethyl is immediately decomposed by an alcoholic solution of potassa, and in the aqueous solution is insoluble, yet it must be an amid-like body  $C_4H_5O + C_4H_3O_2$ ; that compounds also exist of oxide of ethyl with phosphoric, carbonic, boracic, and silicic acid, and that, according to this opinion, basic silicate of ethyl  $3AcO + SiO_3$  consists of  $3(C_4H_5O_2) + Si$ , and, consequently, the alcohol must reduce the silicic acid, which, as is well known, the most violent heating of it with charcoal cannot accomplish; these are facts, left quite out of view. To such hypotheses we arrive, when in judging of the rational constitution of organic compounds, individual phenomena alone, and not their totality, are considered. Whether ether is the same substance which occurs in alcohol and the compound ethers, is, as respects the theory of the organic radicals, a secondary question. For who knows sulphuric acid and potassa in sulphate of potassa? The fact is, that ether and anhydrous sulphuric acid give sulphate of ethyl, in the same manner as sulphuric acid and potassa, the product which we call sulphate of potassa.

This work will be closely allied to my Chemistry of Organic Combinations, to which it will be, as it were, an introduction. Therefore I have not given the per cent. constitution of the individual substances, but only their formulæ: for this reason, also, the discoverers of the same are not mentioned. I have seldom

given the explanation of the chemical processes, leaving that for the meditation of the student. The perfect scientific keeping of the work forbids giving any especial regard to the practical part of organic chemistry; therefore I have directed the attention thereto, by placing those subjects in brackets.

In these *Principles*, it is quite apparent that each specialty cannot be considered. Should any one miss a few of the latest discoveries, it may serve as my excuse that the greater part of the labor of this work was performed in 1850; the General Part, especially, was written long before Kolbe made known his views upon the constitution of the organic compounds. Indeed, I fear more complaint will be made of the *too-much*, than of the *too-little*.

And now little volume go forth into the world, and give friendly greeting to the chemical public.

LÖWIG.

*Zurich*, October 1851.



# TABLE OF CONTENTS.

## GENERAL PART.

IN THE FORMULÆ, X IS PLACED FOR NO<sub>4</sub>.

### CONSTITUTION OF THE ORGANIC COMPOUNDS AND COMPARISON WITH THE INORGANIC.

	PAGE
ELEMENTS of organic compounds . . . . .	33
Atomic proportions of organic compounds . . . . .	33
Empirical formulæ and rational . . . . .	34
Idea of a radical . . . . .	34
Simple radicals . . . . .	34
Substitution of elements . . . . .	35
Compound radicals . . . . .	35
Primary radicals and derived . . . . .	36
Names and symbols of radicals . . . . .	37
Division of compound radicals . . . . .	38
Organic molecules . . . . .	38
Simple organic radicals . . . . .	39
Paired radicals . . . . .	39
Double radicals . . . . .	39
Isomeric, polymeric, and metameric radicals . . . . .	39
Task of organic chemistry . . . . .	40
Isolation of radicals . . . . .	40
Affinity between the elements of organic radicals and compounds . . . . .	40
Primitive affinity . . . . .	41
Original affinity modified by chemical character . . . . .	41
FORMATION OF ORGANIC COMBINATIONS . . . . .	42
1. By decomposition of organic compounds . . . . .	42
<i>a.</i> By the vitality of plants . . . . .	42
<i>b.</i> Without the vitality of plants; artificial formation . . . . .	43
2. By decomposition of already existing organic bodies . . . . .	44
<i>a.</i> By transposition of elements . . . . .	45
Formation of metameric bodies . . . . .	45
<i>b.</i> By increase of original affinity . . . . .	45
1. Without the co-operation of chemically reacting matter . . . . .	46
<i>a.</i> By electrical influence . . . . .	46
<i>b.</i> By the influence of heat . . . . .	47
Action of heat . . . . .	47
Decomposition of non-nitrogenous bodies . . . . .	48
Decomposition of nitrogenous bodies . . . . .	50
Dry distillation . . . . .	51
Combustion . . . . .	51
<i>c.</i> By putrefaction and fermentation . . . . .	52
Vinous fermentation . . . . .	53

	PAGE
Ferment. Yeast . . . . .	54
Decomposed yeast . . . . .	54
Nature of yeast . . . . .	54
Destruction of the power to produce fermentation . . . . .	54
Lactic acid fermentation and butyric acid fermentation . . . . .	55
Fermentation of urea . . . . .	55
Bitter almond oil fermentation . . . . .	55
Mustard oil fermentation . . . . .	55
Saligenin fermentation . . . . .	55
Action of diastase upon starch . . . . .	56
Theories of fermentation . . . . .	56
Evolution of heat by fermentation and putrefaction . . . . .	57
Fermentation and putrefaction under co-operation of oxygen . . . . .	57
Corruption, mouldering, and slow combustion . . . . .	57
Under co-operation of ferment and platinum . . . . .	58
Acetic fermentation . . . . .	58
d. Decomposition by the vital process of the animal organism . . . . .	58
Process of assimilation . . . . .	58
Process of decomposition . . . . .	58
Co-operation of oxygen . . . . .	58
Animal heat . . . . .	59
2. Under co-operation of chemically acting substances . . . . .	59
a. By oxygen . . . . .	59
b. By the halogens . . . . .	60
c. By oxidizing compounds . . . . .	60
d. By reducing matters . . . . .	60

### CONSTITUTION OF ORGANIC RADICALS.

Different groups . . . . .	61
Constitution of the hydrocarbyls . . . . .	62
Their component and active part; nucleus . . . . .	62
Divisions of hydrocarbyls; . . . . .	62
1. Hydroisocarbyls, . . . . .	62
2. Hydropolycarbyls . . . . .	62
I. HYDROISOCARBYLS; they separate into . . . . .	62
a. <i>The Methyl Group</i> : component $\text{xC}_2\text{H}_2$ , active part H . . . . .	62
b. <i>Formyl Group</i> : component $\text{xC}_2\text{H}_2$ , active part $\text{C}_2\text{H}$ . . . . .	62
Conversion of these groups into each other . . . . .	64
Conversion of primary radicals into derived . . . . .	65
Paired radicals formed by the union of the radicals of both groups . . . . .	67
Elayl group . . . . .	68
Acetonyl group . . . . .	68
II. HYDROPOLYCARBYLS.	
a. <i>Oleyl Group</i> . Component, $\text{xC}_2\text{H}_2$ ; Nucleus, $\text{C}_2$ ; Active Part, $\text{C}_2\text{H}$ . . . . .	70
Double radicals consisting of the radicals of the oleyl group with formyl . . . . .	70
Succyl group . . . . .	70
b. <i>Nicyl group</i> ; Component, $\text{xC}_2\text{H}_2$ ; Nucleus, $\text{C}_6$ ; Active Part, H . . . . .	71
c. <i>Niceyl group</i> ; Component, $\text{xC}_2\text{H}_2$ ; Nucleus, $\text{C}_6$ ; Active Part, $\text{C}_2\text{H}$ . . . . .	71
Paired radicals of the nicyl group and the niceyl group . . . . .	71
Furfurol, salicyl, coumaryl . . . . .	72
Anisyl, chinon, phenol, anisol, phenetol . . . . .	73
Derived radicals of these groups . . . . .	74
d. <i>Benzid group</i> ; Component, $\text{xC}_2\text{H}_2$ ; Nucleus, $\text{C}_3$ ; Active Part H . . . . .	75
e. <i>Benzoyl group</i> ; Component, $\text{xC}_2\text{H}_2$ ; Nucleus, $\text{C}_3$ ; Active Part, $\text{C}_2\text{H}$ . . . . .	75
Conversion of the benzoyl group into the benzid group and the reverse . . . . .	75
Derived radicles of these groups . . . . .	75

	PAGE
Paired radicals of the benzyd group . . . . .	76
Picramyl, cinnamyl, cinnamid . . . . .	76
Naphthalin, anthracin, chrysen . . . . .	77
<i>Sulphur combinations, and paired sulphur acids</i> . . . . .	77
<i>Compounds of hydrogen, and radicals which contain H as active element</i> . . . . .	79
<i>a. Nitrogen compounds</i> . . . . .	79
Nitryl, imide, amide, amid acids . . . . .	80
Simple nitrogen bases, ammonia bases, methyl bases, ethyl bases, amyl bases, and anilin bases . . . . .	81
Substitutions of these bases . . . . .	82
Paired nitrogen bases . . . . .	82
Appendix to these . . . . .	82
Glycocol, alanin, leucin, asparagin . . . . .	83
<i>b. Phosphorus, arsenic, and antimony bases</i> . . . . .	84
Compounds of unknown constitution . . . . .	84
<i>a. Carbohydrates</i> . . . . .	85
<i>b. Protein compounds and membranes affording glue</i> . . . . .	85
<i>c. Special vegetable and animal matter</i> . . . . .	85
Some general relations of organic compounds . . . . .	86
Metameric compounds . . . . .	86
Point of ebullition . . . . .	87
Atomic volume of fluid bodies . . . . .	89
Atomic volume of gasiform bodies . . . . .	90
Behavior to light . . . . .	91
<i>a. Power of refraction</i> . . . . .	91
<i>b. Circular polarization</i> . . . . .	91

## SPECIAL PART.

## I. HYDROCARBYLS.

HYDROISOCARBYLS . . . . .	92
1. <i>Methyl Group</i> : general formula; Component, $x\text{C}_2\text{H}_2$ ; Active part II . . . . .	92
<i>Methyl</i> : $\text{Me}=\text{C}_2\text{H}_2, \text{H}=\text{C}_2\text{H}_3$ . . . . .	95
Hydro-methyl: $\text{MeH}$ . . . . .	95
Oxide of methyl: $\text{MeO}$ . . . . .	96
Oxhydrate of methyl: $\text{MeO}, \text{HO}$ . . . . .	96
Carbonate of methyl: $\text{MeO}, \text{CO}_2$ . . . . .	97
Sulphocarbonate of methyl: $\text{MeO}, \text{CS}_2$ . . . . .	97
Basic borate of methyl: $3\text{MeOBoO}_3$ . . . . .	97
Acid borate of methyl: $\text{MeO}, 2\text{BoO}_3$ . . . . .	97
Nitrate of methyl: $\text{MeO}, \text{NO}_5$ . . . . .	97
Sulphate of methyl: $\text{MeO}, \text{SO}_3$ . . . . .	98
Sulphomethylan: $\text{NH} + \text{MeO}, \text{SO}_3$ . . . . .	98
Sulphomethyl-sulphuric acid: $\text{HO}, (\text{Me}, \text{SO}_2) \text{SO}_3$ . . . . .	98
Methyloxyd-carbonic acid: $\text{HO}, (\text{MeO}, \text{CO}_2) \text{CO}_2$ . . . . .	98
Methyloxyd-chlorcarbonic acid: $\text{HO}, (\text{MeO}, \text{CO}_2) \text{C} \begin{Bmatrix} \text{O} \\ \text{Cl} \end{Bmatrix}$ . . . . .	98
Methyloxyd-sulphocarbonic acid: $\text{HO}, (\text{MeO}, \text{CS}_2) \text{CS}_2$ . . . . .	99
Methyloxyd-sulphuric acid: $\text{HO}, (\text{MeO}, \text{SO}_3) \text{SO}_3$ . . . . .	99
Protosulphide of methyl: $\text{MeS}$ . . . . .	99
Sulphocarbonate of sulphide of methyl: $\text{MeS}, \text{CS}_2$ . . . . .	99
Bisulphide of methyl: $\text{MeS}_2$ . . . . .	99
Tersulphide of methyl: $\text{MeS}_3$ . . . . .	99

	PAGE
Methyl-hydrosulphuric acid: $\text{H}(\text{MeS})\sim\text{S}$	99
Iodide of methyl: $\text{MeI}$	99
Bromide of methyl: $\text{MeBr}$	100
Chloride of methyl: $\text{MeCl}$	100
Fluoride of methyl: $\text{MeFl}$	100
<i>Ethyl</i> : $\text{Ae}=\text{2C}_2\text{H}_5, \text{H}=\text{C}_4\text{H}_5$	100
Hydroethyl: $\text{AeH}$	101
Oxide of ethyl: $\text{AeO}$	101
Oxyhydrate of ethyl: $\text{AeO}, \text{HO}$	102
Carbonate of ethyl: $\text{AeO}, \text{CO}_2$	104
Sulphocarbonate of ethyl: $\text{AeO}, \text{CS}_2$	104
Borates of ethyl: $\text{AeO}, 2\text{BoO}_3$ and $3\text{AeO}, \text{BoO}_3$	105
Silicates of ethyl: $3\text{AeO}, \text{SiO}_3$ ; $3\text{AeO}, 2\text{SiO}_3$ ; $3\text{AeO}, 4\text{SiO}_3$	105
Phosphite of ethyl: $2\text{HO}, \text{AeO}, \text{PO}_3$	105
Triphosphate of ethyl: $3\text{AeO}, \text{PO}_5$	105
Diphosphate of ethyl: $\text{HO}, 2\text{AeO} + \text{PO}_5$	105
Ether-phosphoric acid: $2\text{HO}, \text{AeO}, \text{PO}_5$	105
Ether-sulpho-phosphoric acid: $2\text{HO}, \text{AeO}, \text{PO}_3\text{S}_2$	106
Nitrite of ethyl: $\text{AeO}, \text{NO}_3$	106
Nitrate of ethyl: $\text{AeO}, \text{NO}_5$	106
Sulphite of ethyl: $\text{AeO}, \text{SO}_3$	106
Sulphate of ethyl: $\text{AeO}, \text{SO}_3$	106
Hyperchlorate of ethyl: $\text{AeO}, \text{ClO}_7$	106
Sulphethyl-sulphuric acid: $\text{HO}, (\text{Ae}, \text{SO}_2)\sim\text{SO}_3$	106
Ether-carbonic acid: $\text{HO}(\text{AeO}, \text{CO}_2)\text{CO}_2$	107
Ether-oxychlorcarbonic acid: $\text{HO}(\text{AeO}, \text{CO}_2)\sim\text{CO}, \text{Cl}$	107
Ether-sulpho-carbonic acid: $\text{HO}(\text{AeO}, \text{CS}_2)\sim\text{CS}_2$	107
Sulphocarbonate of bioxide of ethyl: $\text{AeO}_2, \text{C}_2\text{S}_4\text{O}$	107
Ether-sulphuric acid: $\text{HO}(\text{AeO}, \text{SO}_3)\sim\text{SO}_3$	108
Sulphide of ethyl: $\text{AeS}$ ; $\text{AeS}_2$ ; $\text{AeS}_3$	109
Sulphocarbonate of sulph-ethyl: $\text{AeS}, \text{CS}_2$	109
Selen-ethyl: $\text{AeSe}$	110
Tellur-ethyl: $\text{AeTe}$	110
Ethyl-hydrosulphuric acid: $\text{H}, (\text{AeS})\sim\text{S}$	110
Potassium-sulph-ethyl: $\text{K}(\text{AeS})\sim\text{S}$	110
Ethyl-selen-hydric acid: $\text{H}(\text{AeSe})\sim\text{Se}$	110
Iodide of ethyl: $\text{AeI}$	111
Bromide of ethyl: $\text{AeBr}$	111
Chloride of ethyl: $\text{AeCl}$	111
Fluoride of ethyl: $\text{AeFl}$	111
<i>Valyl</i> : $\text{Vl}=\text{4C}_2\text{H}_5, \text{H}=\text{C}_8\text{H}_9$	111
<i>Propyl</i> : $\text{Pp}=\text{3C}_2\text{H}_5, \text{H}=\text{C}_6\text{H}_7$	112
<i>Amyl</i> : $\text{Am}=\text{5C}_2\text{H}_5, \text{H}=\text{C}_{10}\text{H}_{11}$	112
Hydroamyl: $\text{AmH}$	112
Oxide of amyl: $\text{AmO}$	112
Oxyhydrate of amyl: $\text{AmO}, \text{HO}$	113
Borate of amyl: $\text{AmO}, 2\text{BoO}_3$	113
Silicate of amyl: $3\text{AmO} + \text{SiO}_3$	113
Nitrite of amyl: $\text{AmO}, \text{NO}_3$	113
Nitrate of amyl: $\text{AmO}, \text{NO}_5$	113
Sulph-amyl-sulphuric acid: $\text{HO}, (\text{Am}, \text{SO}_2)\sim\text{SO}_3$	113
Amyloxyl-sulphocarbonic acid: $\text{HO}(\text{Am}, \text{CS}_2)\sim\text{CS}_2$	114
Amyloxyl-sulphuric acid: $\text{HO}(\text{Am}, \text{SO}_3)\sim\text{SO}_3$	114
Sulphide of amyl: $\text{AmS}$ ; $\text{AmS}_2$	114
Amyl-sulph-hydric acid: $\text{H}(\text{AmS})\sim\text{S}$	114
Iodide of amyl: $\text{AmI}$	114
Bromide of amyl: $\text{AmBr}$	114
Chloride of amyl: $\text{AmCl}$	114
<i>Caproyl</i> : $\text{Cpr}=\text{6C}_2\text{H}_5, \text{H}=\text{C}_{12}\text{H}_{13}$	114
<i>Cethyl</i> : $\text{Ce}=\text{16C}_2\text{H}_5, \text{H}=\text{C}_{32}\text{H}_{33}$	115
Oxyhydrate of cethyl: $\text{CeO}, \text{HO}$	115

	PAGE
Cethyloxyd-sulpho-carbonic acid: $\text{HO}(\text{CeO}, \text{CS}_2) \sim \text{CS}_2$	115
Cethyloxyd-sulphuric acid: $\text{HO}(\text{CeO}, \text{SO}_3) \sim \text{SO}_3$	115
Chloride of cethyl: $\text{CeCl}$	115
<i>Cerossyl</i> : $\text{Cy} = 24\text{C}_2\text{H}_2, \text{H} = \text{C}_{48}\text{H}_{49}$	115
Hydrate of Cerossyl: $\text{CyO}, \text{HO}$	115
<i>Cerotyl</i> : $\text{Cr} = 27\text{C}_2\text{H}_2, \text{H} = \text{C}_{54}\text{H}_{55}$	116
Cerosinic acid: $\text{HO}(\text{C}_{38}\text{H}_{47})\text{O}_3$	116
Oxyhydrate of cerotyl: $\text{CrO}, \text{HO}$	116
<i>Melissyl</i> : $\text{My} = 30\text{C}_2\text{H}_2, \text{H} = \text{C}_{60}\text{H}_{61}$	116
Oxyhydrate of melissyl: $\text{MyO}, \text{HO}$	116
2. <i>Formyl group</i> ; general formula: Component, $\text{xC}_2\text{H}_2$ ; Active part, $\text{C}_2\text{H}$	117
1. <i>Formyl</i> : $\text{Fo} = \text{C}_2\text{H}$	119
Formic acid: hydrate of $\text{HO}, \text{FoO}_3$	119
Formyl: sulphide $\text{FoS}_3$	120
Formyl: iodide $\text{FoI}_3$	120
Formyl: bromide $\text{FoBr}_3$	121
Formyl: chloride $\text{FoCl}$	121
Formyl: bichloride $\text{FoCl}_2$	121
Formyl: terchloride $\text{FoCl}_3$	121
Formyl: oxychloride $\text{FoOCl}_2$	121
Formyl: sulphochloride $\text{FoSCl}_2$	122
Formyl: iodochloride $\text{FoICl}_2$	122
Formyl: bromiodide $\text{FoBrI}_2$	122
Formyl: formate of oxychloride $\text{FoOCl}, \text{FoO}_3$	122
Formyl-sulphochloride-sulphuric acid: $\text{HO}, (\text{FoCl}_2, \text{SO}_2) \sim \text{SO}_3$	122
Derived radicals of formyl	122
2. Chlorformyl: $\text{C}_2\text{Cl}$	122
Chlorformic acid: $(\text{ClFo})\text{O}_3$	122
Chlorformyl: chloride of $(\text{ClFo})\text{Cl}_3$	122
Chlorformyl: oxychloride $(\text{ClFo})\text{OCl}_2$	123
Chlorformyl: sulphochloride $(\text{ClFo})\text{SCl}_2$	123
Chlorformyl: chlorosulphide $(\text{ClFo})\text{ClS}_2$	123
Chlorformyl: chlorformate of oxychloride $\text{ClFoOCl}_2, \text{ClFoO}_3$	123
Chlorformyl: sulphite of chloride $\text{ClFoCl}, 2\text{SO}_2$	123
Chlorformyl: sulphite of terchloride $\text{ClFoCl}_3, 2\text{SO}_2$	123
Chlorformyl-sulphochlorid-sulphuric acid: $\text{HO}(\text{ClFoCl}_2, \text{SO}_2) \sim \text{SO}_3$	124
Chlor-elayl-hyposulphuric acid: $2\text{HO}(\text{ClFoCl}_2, \text{SO}_2) \sim \text{SO}_3 + (\text{Me}, \text{SO}_2) \sim \text{SO}_3$	124

PAIRED RADICALS, CONSISTING OF THE RADICALS OF THE METHYL GROUP  
AND FORMYL.

<i>The Elayl Group</i>	124
<i>Methylen</i> : $\text{H}, \sim \text{Fo} = \text{H}, \sim \text{C}_2\text{H} = \text{C}_2\text{H}_2$	125
<i>Elayl</i> : $\text{Me}, \sim \text{Fo} = \text{C}_2\text{H}_3, \text{C}_2\text{H} = \text{C}_4\text{H}_4$	125
Elayl: bisulphide $\text{MeS} \sim \text{FoS}$	125
Elayl: tetrasulphide $\text{MeS}, \sim \text{FoS}_3$	125
Elayl-hydrosulphuric acid: $\text{H}_2(\text{MeS}, \sim \text{FoS})\text{S}_2$	126
Elayl: iodide of $\text{MeI}, \sim \text{FoI}$	126
Elayl: bromide $\text{MeBr}, \sim \text{FoBr}$	126
Elayl: chloride $\text{MeCl}, \sim \text{FoCl}$	126
Methylen-formyl: protochloride of $(\text{H}, \sim \text{C}_2\text{H} + \sim \text{C}_2\text{H})\text{Cl}$	126
Methylen-formyl: terchloride of $(\text{H}, \sim \text{C}_2\text{H} \sim \text{C}_2\text{H})\text{Cl}$	127
Elayl: oxychloride of $\text{MeO}, \sim \text{FoCl}$	127
Elayl-platinum	127
Elayl: sulphate of $\text{MeSO}_3, \sim \text{Fo}, \text{SO}_3$	127
Elayl-sulphuric acid: $(\text{C}_2\text{H}_3, \text{SO}_3 \sim \text{C}_2\text{H}, \text{SO}_3) \sim 2\text{SO}_3$	127
Isäthionic acid: $\text{HO}, (\text{H} \sim \text{Fo}, \sim \text{MeO}, \text{SO}_3)\text{SO}_3$	127
Elayl: ether-sulphate of $2(\text{AeO}, \text{SO}_3) + (\text{MeSO}_3, \sim \text{FoSO}_3)$	128
<i>Propylen</i> : $\text{Ac}, \sim \text{Fo} = \text{C}_4\text{H}_5, \sim \text{C}_2\text{H} = \text{C}_6\text{H}_6$	128
Bromide of propylen: $\text{AeBr}, \sim \text{FoBr}$	128
Bromide of acetyl-formyl: $\text{AcBr}, \sim \text{FoBr}; \text{AcBr} \sim \text{FoBr}_3$	128

	PAGE
Chloride of propylen: $\text{AcCl}, \sim \text{FoCl}$	128
<i>Valylen</i> : $\text{Pp}, \sim \text{Fo}=\text{C}_6\text{H}_7, \text{C}_2\text{H}=\text{C}_8\text{H}_8$	128
Bichloride of valylen: $\text{PpCl}, \text{FoCl}$	129
<i>Amylen</i> : $\text{Vl}, \sim \text{Fo}=\text{C}_8\text{H}_9, \text{C}_2\text{H}=\text{C}_{10}\text{H}_{10}$	129
<i>Oleen</i> : $\text{Am}, \sim \text{Fo}=\text{C}_{10}\text{H}_{11}, \sim \text{C}_2\text{H}=\text{C}_{12}\text{H}_{12}$	129
Chloride of Oleen: $\text{AmCl}, \sim \text{FoCl}$	129
<i>Elaen</i> : $\text{Ca}, \sim \text{Fo}=\text{C}_{14}\text{H}_{15}, \sim \text{C}_2\text{H}=\text{C}_{16}\text{H}_{16}$	129
Paramylen: $\text{C}_{20}\text{H}_{20}$ ; Ceten: $\text{C}_{32}\text{H}_{32}$	129
Metamylen: $\text{C}_{40}\text{H}_{40}$	129
Ceroten: $\text{C}_{54}\text{H}_{54}$ ; Melissen: $\text{C}_{60}\text{H}_{60}$ , etc.	129
<i>Acetyl</i> : $\text{Ac}=\text{C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_4\text{H}_3$	130
Oxide of acetyl: $\text{AcO}$	130
Oxyhydrate of acetyl: $\text{HO}, \text{AcO}$	130
Potassa-acetyloxyd: $\text{KO}, \text{AcO}$	131
Aldehyd-ammonia: $\text{NH}_4\text{O}, \text{AcO}$	131
Metaldehyd: $\text{C}_{12}\text{H}_{12}\text{S}_6$	131
Hydrosulphometaldehyd: $\text{C}_{12}\text{H}_{12}\text{S}_6 + \text{HS}$	131
Sulphometaldehyd: $\text{C}_{12}\text{H}_{12}\text{S}_6$	131
Carbothialdin: $\text{NC}_5\text{H}_5\text{S}_2=\text{NH}_3, \sim (\text{C}_4\text{H}_5, \text{CS}_2)$	132
Acetic acid: $\text{AcO}_3$	132
Hydrate of acetic acid: $\text{HO}, \text{AcO}_3$	132
Salts of acetic acid	133
Oxysulphide of acetyl: $\text{AcOS}_2$	135
Chloride of acetyl: $\text{AcCl}_3$	135
Oxychloride of acetyl: $\text{AcOCl}_2$	135
Oxysulphochloride of acetyl: $\text{AcOSEl}$	135
Carbonate of oxychloride of acetyl: $\text{AcOCl}_2, \text{CO}_2$	135
Formate of oxychloride of acetyl: $\text{AcOCl}_2, \text{FoO}_3$	136
Acetate of oxychloride of formyl: $\text{FoOCl}_2, \text{AcO}_3$	136
Acetate of oxychloride of acetyl: $\text{AOCl}_2, \text{AcO}_3$	136
Acetate of oxychloride of chlorformyl: $\text{ClFoOCl}_2, \text{AcO}_3$	136
Nitro-acetyl: $\text{AcN}$	136
Chlorplatin-acetylchloride: $(\text{Ac}, \sim \text{PtCl}) \sim \text{PtCl}$	136

## DERIVED RADICALS OF ACETYL.

2. <i>Bichloracetyl</i> : $\text{Cl}_3\text{Ac}=\text{C}_2\text{Cl}_2, \text{C}_2\text{H}=\text{C}_4\text{Cl}_2\text{H}$	137
Bichloracetic acid: $\text{Cl}_3\text{AcO}_3$	137
Bichloracetate of oxychloride of formyl: $\text{FoOCl}_2, \text{Cl}_3\text{AcO}_3$	137
Bichloracetate of oxychloride of chlorformyl: $\text{ClFoOCl}_2, \text{Cl}_3\text{AcO}_3$	137
Formate of oxychloride of bichloracetyl: $\text{ClAcOCl}_2, \text{FoO}_3$	137
Acetate of oxychloride of bichloracetyl: $\text{Cl}_3\text{AcOCl}_2, \text{AcO}_3$	137
3. <i>Chloracetyl</i> : $\text{Cl}_3\text{Ac}=\text{C}_2\text{Cl}_2, \text{C}_2\text{Cl}=\text{C}_4\text{Cl}_3$	137
Oxide of chloracetyl: $\text{Cl}_3\text{AcO}$	137
Oxyhydrate of chloracetyl: $\text{HO}, \text{Cl}_3\text{AcO}$	138
Chloralid: $\text{C}_{10}\text{H}_7\text{Cl}_6\text{O}_2$	138
Chloracetic acid: $\text{Cl}_3\text{AcO}_3$	138
Hydrate of chloracetic acid: $\text{HOCl}_3\text{AcO}_3$	138
Chloride of chloracetyl: $\text{Cl}_3\text{AcCl}$	139
Chlorobromide of chloracetyl: $\text{Cl}_3\text{AcClBr}_2$	139
Terchchloride of chloracetyl: $\text{Cl}_3\text{AcCl}_3$	139
Oxychloride of chloracetyl: $\text{Cl}_3\text{AcO}_2\text{Cl}$	139
Oxybichloride of chloracetyl: $\text{Cl}_3\text{AcOCl}_2$	140
Sulphochloride of chloracetyl: $\text{Cl}_3\text{AcSCl}_2$	140
Oxybromide of chloracetyl: $\text{Cl}_3\text{AcOBr}_2$	140
Chlorbromide of chloracetyl: $\text{Cl}_3\text{AcClBr}_2$	140
Carbonate of oxybichloride of chloracetyl: $\text{Cl}_3\text{AcOCl}_2, \text{CO}_2$	140
Formate of oxybichloride of chloracetyl: $\text{Cl}_3\text{AcOCl}_2, \text{FoO}_3$	141
Chlorformate of oxybichloride of chloracetyl: $\text{Cl}_3\text{AcOCl}_2, \text{Cl}_3\text{FoO}_3$	141
Acetate of oxybichloride of chloracetyl: $\text{Cl}_3\text{AcOCl}_2, \text{AcO}_3$	141
Bichloracetate of oxybichloride of chloracetyl: $\text{Cl}_3\text{AcOCl}_2, \text{Cl}_3\text{AcO}_3$	141
Chloracetate of oxybichloride of chloracetyl: $\text{Cl}_3\text{AcOCl}_2, \text{Cl}_3\text{AcO}_3$	141
Nitrochloracetyl: $\text{Cl}_3\text{AcN}$	141



	PAGE
4. <i>Bromacetyl</i> : $\text{Br}_3\text{Ac}=\text{C}_2\text{Br}_2, \text{C}_2\text{Br}=\text{C}_4\text{Br}_3$ . . . . .	141
Oxyhydrate of bromacetyl: $\text{HO}, \text{Br}_3\text{AcO}_3$ . . . . .	141
5. <i>Iodacetyl</i> : $\text{I}_3\text{Ac}=\text{C}_2\text{I}_2, \text{C}_2\text{I}=\text{C}_4\text{I}_3$ . . . . .	142
Oxyhydrate of iodacetyl: $\text{HO}, \text{I}_3\text{AcO}_3$ . . . . .	142
6. <i>Sulphacetyl</i> : $\text{SO}_2\text{Ac}=\text{C}_2\text{H}_2, \text{C}_2\text{SO}_2=\text{C}_4\text{H}_2\text{SO}_2$ . . . . .	142
Sulphacetyl-sulphuric acid: $2\text{HO}, \text{SO}_2\text{AcO}_3, \text{SO}_3$ . . . . .	142

## PAIRED RADICALS OF ACETYL.

<i>Acryl</i> : $\text{AcrC}_2, \text{C}_4\text{H}_3=\text{C}_6\text{H}_3$ . . . . .	142
Oxyhydrate of Acryl: $\text{HO}, \text{AcrO}$ . . . . .	142
Acrolein-ammonia: $\text{NH}_4, \text{O}+\text{AcrO}$ . . . . .	143
Hydrate of acrylic acid: $\text{HO}, \text{AcrO}_3$ . . . . .	143
Diacryl: $\text{C}_{10}\text{H}_7\text{O}_4$ . . . . .	143
<i>Lactyl</i> : $\text{Lac}=\text{C}_4\text{H}_2\text{O}_2, \text{C}_4\text{H}_3=\text{C}_6\text{H}_5\text{O}_2$ . . . . .	143
Lactic acid: $\text{LacO}_3$ . . . . .	143
Hydrate of lactic acid: $\text{HO}, \text{LacO}_3$ . . . . .	144
Lactid: $\text{C}_6\text{H}_4\text{O}_4$ . . . . .	144
<i>Chlorsuccyl</i> : $\text{Cl}_3\text{Su}=\text{C}_2\text{H}_2, \text{C}_4\text{H}_3=\text{C}_6\text{H}_2\text{Cl}_3$ . . . . .	144
Chlorsuccinic acid: $\text{Cl}_3\text{SuO}_3$ . . . . .	144
Double radicals of methyl with acetyl . . . . .	145
<i>Acetonyl</i> : $\text{Me}, \text{Ac}=\text{C}_2\text{H}_3, \text{C}_4\text{H}_3=\text{C}_6\text{H}_6$ . . . . .	145
Oxide of acetonyl: $\text{MeO}, \text{AcO}=\text{C}_6\text{H}_6\text{O}_2$ . . . . .	145
<i>Propionyl</i> : $\text{Pr}=\text{C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_6\text{H}_5$ . . . . .	147
Oxyhydrate of propionyl: $\text{HO}, \text{PrO}$ . . . . .	147
Hydrate of propionic acid: $\text{HO}, \text{PrO}_3$ . . . . .	147
Propion: $\text{AcO}, \text{PrO}=\text{C}_{10}\text{H}_{10}\text{O}_2$ . . . . .	148
1. <i>Butyryl</i> : $\text{Bu}=\text{C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_8\text{H}_7$ . . . . .	148
Oxyhydrate of butyryl: $\text{HO}, \text{BuO}$ . . . . .	148
Oxide of butyryl: $\text{BuO}$ . . . . .	148
Butyric acid: $\text{BuO}_3$ . . . . .	148
Hydrate of butyric acid: $\text{HO}, \text{BuO}_3$ . . . . .	148
Derived radicals of butyryl . . . . .	150
2. <i>Bichlorobutyryl</i> : $\text{Cl}_2\text{Bu}=\text{C}_2\text{H}_2, \text{C}_2\text{Cl}_2, \text{C}_2\text{H}=\text{C}_3\text{H}_5\text{Cl}_2$ . . . . .	150
Oxyhydrate of bichlorobutyryl: $\text{HO}, \text{Cl}_2\text{BuO}$ . . . . .	150
Hydrate of bichlorobutyric acid: $\text{HO}, \text{Cl}_2\text{BuO}_3$ . . . . .	150
3. <i>Quadrichlorobutyryl</i> : $\text{Cl}_4\text{Bu}=\text{C}_2\text{H}_2, 2\text{C}_2\text{Cl}_2, \text{C}_2\text{H}=\text{C}_3\text{H}_3\text{Cl}_4$ . . . . .	150
Oxyhydrate of quadrichlorobutyryl: $\text{HO}, \text{Cl}_4\text{BuO}$ . . . . .	150
Hydrate of quadrichlorobutyric acid: $\text{HO}, \text{Cl}_4\text{BuO}_3$ . . . . .	150
Butyron: $\text{PpO}, \text{BuO}=\text{C}_{14}\text{H}_{14}\text{O}_2$ . . . . .	150
1. <i>Valeryl</i> : $\text{Va}=\text{C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{10}\text{H}_9$ . . . . .	150
Oxide of valeryl: $\text{VaO}$ . . . . .	151
Oxyhydrate of valeryl: $\text{HO}, \text{VaO}$ . . . . .	151
Valerianic acid: $\text{VaO}_3$ . . . . .	151
Hydrate of valerianic acid: $\text{HO}, \text{VaO}_3$ . . . . .	151
Acetate of oxychloride of valeryl: $\text{VaOCl}_2, \text{AcO}_3$ . . . . .	152
Derived radicals of valeryl . . . . .	152
2. <i>Bichlor-valeryl</i> : $\text{Cl}_2\text{Va}=\text{C}_2\text{H}_2, \text{C}_2\text{Cl}_2, \text{C}_2\text{H}=\text{C}_{10}\text{H}_7\text{Cl}_2$ . . . . .	152
Hydrate of bichlor-valerianic acid: $\text{HO}, \text{Cl}_2\text{VaO}_3$ . . . . .	152
3. <i>Quadrichlor-valeryl</i> : $\text{Cl}_4\text{Va}=\text{C}_2\text{H}_2, 2\text{C}_2\text{Cl}_2, \text{C}_2\text{H}=\text{C}_{10}\text{H}_5\text{Cl}_4$ . . . . .	152
Hydrate of quadrichlor-valerianic acid: $\text{HO}, \text{Cl}_4\text{VaO}_3$ . . . . .	152
4. <i>Hexachlor-valeryl</i> : $\text{Cl}_6\text{Va}=\text{C}_2\text{H}_2, 3\text{C}_2\text{Cl}_2, \text{C}_2\text{H}=\text{C}_{10}\text{H}_3\text{Cl}_6$ . . . . .	152
Terchloride of hexachlor-valeryl: $\text{Cl}_6\text{VaCl}_3$ . . . . .	152
Valeron: $\text{VlO}, \text{VaO}=\text{C}_{18}\text{H}_{18}\text{O}_2$ . . . . .	153
<i>Capromyl</i> : $\text{Ca}=\text{C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{12}\text{H}_{11}$ . . . . .	153
Hydrate of capronic acid: $\text{HOCaO}_3$ . . . . .	153
Nitrocapromyl: $\text{CaN}$ . . . . .	153
Capron: $\text{AmO}, \text{CaO}=\text{C}_{22}\text{H}_{22}\text{O}_2$ . . . . .	153
1. <i>Oenanthyl</i> : $\text{Oe}=\text{C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{14}\text{H}_{13}$ . . . . .	154
Oxyhydrate of oenanthyl: $\text{HO}, \text{OeO}$ . . . . .	154
Hydrate of oenanthic acid: $\text{HO}, \text{OeO}_3$ . . . . .	154

	PAGE
Derived radicals of oenanthyl	154
2. Bichloroentanhyll: $\text{Cl}_2\text{Oe}=\text{5C}_2\text{H}_2, \text{C}_2\text{Cl}_2, \text{C}_2\text{H}=\text{C}_{14}\text{H}_{11}\text{Cl}_2$	154
3. Quadrichloroentanhyll: $\text{Cl}_4\text{Oe}=\text{4C}_2\text{H}_2, \text{2C}_2\text{Cl}_2, \text{C}_2\text{H}=\text{C}_{14}\text{H}_9\text{Cl}_4$	154
Oxyhydrate of bichloroentanhyll: $\text{HO}, \text{Cl}_2\text{OeO}$	155
Oenanthic acid: $\text{C}_{14}\text{H}_{13}\text{O}_2$	155
Capryll: $\text{Cp}=\text{7C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{16}\text{H}_{15}$	155
Hydrate of capric acid: $\text{HO}, \text{CpO}_3$	155
Pelargonyll: $\text{Pg}=\text{8C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{18}\text{H}_{17}$	155
Hydrate of pelargonic acid: $\text{HO}, \text{PgO}_3$	155
Caprinyll: $\text{Cr}=\text{9C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{20}\text{H}_{19}$	156
Oxyhydrate of caprinyll: $\text{HO}, \text{CrO}$	156
Hydrate of caprinic acid: $\text{HO}, \text{CrO}_3$	156
Oxychloride of caprinyll: $\text{CrOCl}_2$	156
Cocyll: $\text{Co}=\text{10C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{22}\text{H}_{21}$	156
Hydrate of cocylic acid: $\text{HO}, \text{CO}_3$	156
Laurostearyll: $\text{Lro}=\text{11C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{24}\text{H}_{23}$	157
Hydrate of laurostearic acid: $\text{HO}, \text{LroO}_3$	157
Myristicyll: $\text{My}=\text{13C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{28}\text{H}_{27}$	157
Hydrate of myristic acid: $\text{HO}, \text{MyO}_3$	157
Behyll: $\text{By}=\text{14C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{30}\text{H}_{29}$	157
Hydrate of behylic acid: $\text{HO}, \text{ByO}_3$	157
Palmityll: $\text{Pa}=\text{15C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{32}\text{H}_{31}$	157
Hydrate of palmitic acid: $\text{HO}, \text{PaO}_3$	157
Ethalic, olidic, madiac, and bogbutyric acid: $\text{HO}, (\text{C}_{32}\text{H}_{31})\text{O}_3$	157
Margaryll: $\text{Mg}=\text{16C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{34}\text{H}_{33}$	158
Hydrate of margaric acid: $\text{HO}, \text{MgO}_3$	158
Hydrate of stearic acid: $2\text{HO}, \text{Mg}_2\text{O}_5$	160
Margarin-sulphuric acid	161
Metamargaric acid: $\text{HO}(\text{C}_{34}\text{H}_{33})\text{O}_3$	161
Hydromargaric acid: $\text{HO}(\text{C}_{34}\text{H}_{33})\text{O}_4$	161
Hydromargaritic acid: $\text{HO}(\text{C}_{34}\text{H}_{33})\text{O}_5$	161
Margaron: $\text{CeO}, \text{MgO}=\text{C}_{66}\text{H}_{66}\text{O}_2(?)$	162
Stearophanyll: $\text{Sph}=\text{17C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{36}\text{H}_{35}$	162
Hydrate of stearophanic acid: $\text{HO}, \text{SphO}_3$	162
Behenyll: $\text{Bh}=\text{21C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{44}\text{H}_{43}$	162
Hydrate of behenylic acid: $\text{HO}, \text{BhO}_3$	162
Cerossyll: $\text{Cy}=\text{23C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{46}\text{H}_{47}$	162
Hydrate of cerossic acid: $\text{HO}, \text{CyO}_3$	162
Cerotyll: $\text{Ct}=\text{26C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{54}\text{H}_{53}$	162
Hydrate of cerotic acid: $\text{HO}, \text{CtO}_3$	162
Mellissyll: $\text{Ml}=\text{29C}_2\text{H}_2, \text{C}_2\text{H}=\text{C}_{60}\text{H}_{59}$	163
Hydrate of mellissic acid: $\text{HO}, \text{MeO}_3$	163

*Salt-like Combinations of the Oxides of the Methyl Group with the Acids of the Formyl Group.*

Combinations of the oxide of methyl	163
Formate of methyl: $\text{MeO}, \text{FoO}_3$	163
Basic formate of methyl: $3\text{MeO}, \text{FoO}_3$	163
Chlorformate of methyl: $\text{MeO}, \text{ClFoO}_3$	163
Acetate of methyl: $\text{MeO}, \text{AcO}_3$	163
Xylit, mesit	164
Chloracetate of methyl: $\text{MeO}, \text{Cl}_3\text{AcO}_3$	164
Combinations of oxide of ethyl	164
Formate of ethyl: $\text{AeO}, \text{FoO}_3$	164
Chlorformate of ethyl: $\text{AeO}, \text{ClFoO}_3$	164
Acetate of ethyl: $\text{AeO}, \text{AcO}_3$	164
Acetal: $3\text{AeO}, \text{AcO}_3$	164
Chloracetate of ethyl: $\text{AeO}, \text{Cl}_3\text{AcO}_3$	165
Ether-sulphacetic acid: $\text{HO}(\text{AeO}^-\text{SO}_2\text{Ac})^-\text{SO}_3$	165
Acrate of ethyl: $\text{AeO}, \text{AcO}_3$	165

	PAGE
Propionate of ethyl: $\text{AeO}, \text{PrO}_3$ . . . . .	165
Butyrate of ethyl: $\text{AeO}, \text{BuO}_3$ . . . . .	165
Bichlor-butyrate of ethyl: $\text{AeO}, \text{Cl}_2\text{BuO}_3$ . . . . .	165
Valerianate of ethyl: $\text{AeO}, \text{VaO}_3$ . . . . .	165
Capronate of ethyl: $\text{AeO}, \text{CaO}_3$ . . . . .	165
Margarinate of ethyl: $\text{AeO}, \text{MgO}_3$ . . . . .	165
Ether-stearic acid: $\text{AeO}, \text{HO}, \text{Mg}_2\text{O}_5$ , etc. . . . .	166
<i>Combinations of oxide of amyl</i> . . . . .	166
Acetate of amyl: $\text{AmO}, \text{AcO}_3$ . . . . .	166
Valerianate of amyl: $\text{AmO}, \text{VaO}_3$ . . . . .	166
<i>Spermaceti and wax</i> . . . . .	166
Ethalate of cethyl: $\text{CeO}, \text{AeO}_3$ (spermaceti) . . . . .	166
Cerosinate of cerosinyl: $\text{CyO}, \text{CoO}_3$ (cerosin, sugar-cane wax) . . . . .	166
Cerotate of cerotyl: $\text{CrO}, \text{CtO}_3$ (Chinese wax) . . . . .	166
Palmitate of mellissyl: $\text{MyO}, \text{PaO}_3$ (myricin, beeswax) . . . . .	166
Palm wax, cernauba wax: $\text{C}_{36}\text{H}_{36}\text{O}_2$ . . . . .	167
Myrica wax, ocuba wax: $\text{C}_{36}\text{H}_{36}\text{O}_5$ . . . . .	167
Leaf wax, cork wax: $\text{C}_{25}\text{H}_{20}\text{O}_3$ . . . . .	167

## HYDROPOLYCARBYLS.

## FIRST GROUP.

*Carbon Nucleus:  $\text{C}_2$ .*

1. <i>Allyl group.</i> Formula: Component, $\text{x}\text{C}_2\text{H}_2$ ; Nucleus, $\text{C}_2$ ; Active part, H	168
Allyl: $\text{Al}=\text{2C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_5\text{H}_5$ . . . . .	168
Oxide of allyl: $\text{AlO}$ . . . . .	169
Sulphur allyl: $\text{AlS}$ . . . . .	169
Chlor-allyl: $\text{AlCl}$ . . . . .	170
Odmyl: $\text{Od}=\text{3C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_8\text{H}_7$ . . . . .	171
Sulphur-odmyle: $\text{OdS}$ . . . . .	171
Sulpho-hydro-odmyle: $\text{OdS}, \text{HS}$ . . . . .	171
Ferulyl: $\text{Fy}=\text{5C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_{12}\text{H}_{11}$ . . . . .	171
Sulpho-ferrulyl . . . . .	171
2. <i>Oleyl group.</i> Formula: Component, $\text{x}\text{C}_2\text{H}_2$ ; Nucleus, $\text{C}_2$ ; Active part, $\text{C}_2\text{H}$	172
Terecyl: $\text{Tr}=\text{C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_6\text{H}_3$ . . . . .	172
Hydrate of terecic acid: $\text{HO}, \text{TrO}_4(?)$ . . . . .	173
Angelicyl: $\text{Ag}=\text{3C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_{10}\text{H}_7$ . . . . .	173
Hydrate of angelic acid: $\text{HO}, \text{AgO}_3$ . . . . .	173
Moringyl: $\text{Mo}=\text{13C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_{30}\text{H}_{27}$ . . . . .	173
Hydrate of moringa acid: $\text{HO}, \text{MoO}_3$ . . . . .	173
Oleyl: $\text{Ol}=\text{16C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_{36}\text{H}_{33}$ . . . . .	174
Hydrate of oleinic acid (oleic acid): $\text{HO}, \text{OlO}_3$ . . . . .	174
Elaidic acid: $\text{HO}, (\text{C}_{36}\text{H}_{33})\text{O}_3$ . . . . .	174
Olinic acid: $\text{HO}, (\text{C}_{36}\text{H}_{33})\text{O}_3(?)$ . . . . .	174
Olein-sulphuric acid . . . . .	175
Meta-oleic acid . . . . .	175
Hydro-oleic acid . . . . .	175
Doeglyl: $\text{Doe}=\text{17C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_{38}\text{H}_{35}$ . . . . .	175
Hydrate of doeglinic acid: $\text{HO}, \text{DoeO}_3$ . . . . .	175
Hydrate of ricinic acid: $\text{HO}, (\text{C}_{38}\text{H}_{35})\text{O}_5$ . . . . .	175
Erucyl: $\text{Er}=\text{20C}_2\text{H}_2$ , $\text{C}_2\text{H}=\text{C}_{44}\text{H}_{41}$ . . . . .	176
Hydrate of erucaic acid: $\text{HO}, \text{ErO}_3$ . . . . .	176
Salt-like combinations of these acids . . . . .	176
Oleate of ethyl: $\text{AeO}, \text{OlO}_3$ . . . . .	176
Elaidate of ethyl: $\text{AeO}, \text{ElO}_3$ . . . . .	176
Doeglinatate of ethyl: $\text{AeO}, \text{DoeO}_3$ . . . . .	176
<i>Double acids</i> , consisting of the acids of the oleyl group with formic acid . . . . .	176
Succinic acid: $\text{SuO}_6=\text{C}_6\text{H}_3$ , $\text{O}_3$ , $\text{FoO}_3=\text{C}_8\text{H}_4\text{O}_6$ . . . . .	177
Hydrate of succinic acid: $\text{2HO}, \text{SuO}_6$ . . . . .	177
Chlor-succinate of oxychloride of chlor-acetyl: $\text{2(Cl}_3\text{AcOCl}_2)+\text{C}_6\text{Cl}_3\text{O}_3$ , $\text{FoO}_3$ . . . . .	179

	PAGE
Succin-sulphuric acid: $3\text{HO}, (\text{C}_6\text{H}_2\text{O}_2, \text{Fo})\text{O}_3 \sim 2\text{SO}_3$	179
Lipinic acid: $\text{LiO}_6 = \text{C}_8\text{H}_5\text{O}_3, \text{FoO}_3 = \text{C}_{10}\text{H}_6\text{O}_6$	179
Hydrate of lipinic acid: $2\text{HO}, \text{LiO}_6$	179
Adipinic acid: $\text{AdO}_6 = \text{C}_{10}\text{H}_7\text{O}_3, \text{FoO}_3 = \text{C}_{12}\text{H}_8\text{O}_6$	180
Hydrate of adipinic acid: $2\text{HO}, \text{AdO}_6$	180
Pimelinic acid: $\text{PiO}_6 = \text{C}_{12}\text{H}_9\text{O}_3, \text{FoO}_3 = \text{C}_{14}\text{H}_{10}\text{O}_6$	180
Hydrate of pimelinic acid: $2\text{HO}, \text{PiO}_6$	180
Suberic acid: $\text{SbO}_6 = \text{C}_{14}\text{H}_{11}\text{O}_3, \text{FoO}_3 = \text{C}_{16}\text{H}_{12}\text{O}_6$	180
Hydrate of suberic acid: $2\text{HO}, \text{SbO}_6$	180
Sebacic acid: $\text{SeO}_6 = \text{C}_{18}\text{H}_{13}\text{O}_3, \text{FoO}_3 = \text{C}_{20}\text{H}_{16}\text{O}_6$	180
Hydrate of sebacic acid: $2\text{HO}, \text{SeO}_6$	180
<i>Appendix to the succyl group</i>	181
Camphoric acid: $\text{CphO}_6 = \text{C}_{18}\text{H}_{13}\text{O}_3, \text{FoO}_3 = \text{C}_{20}\text{H}_{14}\text{O}_6$	182
Hydrate of camphoric acid: $2\text{HO}, \text{CphO}_6$	182
Phoron: $\text{C}_{18}\text{H}_{14}\text{O}_2$	182
Phtalinic acid: $\text{PthO}_6 = \text{C}_{14}\text{H}_9\text{O}_3, \text{FoO}_3 = \text{C}_{16}\text{H}_4\text{O}_6$	182
Hydrate of phtalinic acid: $2\text{HO}, \text{PthO}_6$	183
Terephthalic acid: $2\text{HO}, \text{C}_6\text{H}_4\text{O}_6$	184
Terebinic acid: $\text{HO}, \text{C}_{14}\text{H}_9\text{O}_7$	184
Pyroterebinic acid: $\text{C}_{12}\text{H}_{10}\text{O}_4$	184
<i>Salt-like combinations of these acids</i>	184
Succinate of methyl: $2\text{MeO}, \text{SuO}_6$	184
Suberate of methyl: $2\text{MeO}, \text{SbO}_6$	184
Succinate of ethyl: $2\text{AeO}, \text{SuO}_6$	184
Suberate of ethyl: $2\text{AeO}, \text{SbO}_6$	185
Adipinate of ethyl: $2\text{AeO}, \text{AdO}_6$	185
Camphorate of ethyl: $2\text{AeO}, \text{CphO}_6$	185
Ether-camphoric acid: $\text{AeO}, \text{HO}, \text{CphO}_6$	185
Phtalinate of ethyl: $2\text{AeO}, \text{PthO}_6$	185

## SECOND GROUP.

*Carbon Nucleus: C<sub>4</sub>.*

<i>Glycyl Group.</i> General formula: Component, $\text{xC}_2\text{H}_2$ ; Nucleus, $\text{C}_4$ ; Active part, H	185
<i>Glycyl:</i> $\text{Gl} = \text{C}_2\text{H}_2, \text{C}_4, \text{H} = \text{C}_6\text{H}_3$	185
Oxide of glycyl: $\text{GlO}$	185
<i>Salt-like combination of oxide of glycyl (Fat)</i>	186
Butyrate of glycyl: $\text{GlO}, \text{BuO}_3$ (Butyrin)	186
Valerianate of glycyl: $\text{GlO}, \text{VaO}_3$ (Delphin)	186
Laurostearinate of glycyl: $\text{GlO}, \text{LauO}_3$ (Laurostearin)	186
Myristicinate of glycyl: $\text{GlO}, \text{MyO}_3$ (Myristicin)	187
Palmitinate of glycyl: $\text{GlO}, \text{PaO}_3$ (Palmitin)	187
Margarinate of glycyl: $\text{GlO}, \text{MgO}_3$ (Margarin)	187
Stearinate of glycyl: $2\text{GlO}, \text{Mg}_2\text{O}_5$ (Stearin)	187
Stearophanate of glycyl: $\text{GlO}, \text{SphO}_3$ (Stearophanin)	187
Oleinate of glycyl: $\text{GlO}, \text{OlO}_3$ (Olein)	187
Olinat of glycyl: $\text{GlO}, \text{OlO}_5$ (Olin, etc.)	187
Fats and oils occurring in Nature	188
Soaps and plasters	189

## THIRD GROUP.

*Carbon Nucleus: C<sub>6</sub>.*

1. <i>Nicid Group.</i> General formula: Component, $\text{xC}_2\text{H}_2$ ; Nucleus, $\text{C}_6$ ; Active part, H	192
<i>Nicid:</i> $\text{Ne} = 2\text{C}_2\text{H}_2, \text{C}_6, \text{H} = \text{C}_{10}\text{H}_5$	192
Chloride of nicid: $\text{NeCl}$	192
Paranicin: $\text{C}_{20}\text{H}_{12}$	192

	PAGE
2. <i>Niceyl Group</i> . General formula: Component, $x\text{C}_2\text{H}_2$ ; Nucleus, $\text{C}_6$ : Active part, $\text{C}_4\text{H}$	192
Niceyl: $\text{Ne}=\text{2C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H}=\text{C}_{12}\text{H}_5$	192
Hydrate of niccinic acid: $\text{HO}, \text{NeO}_3$	192
Chlorniceinic acid: $2\text{HO}, \text{Cl}_2\text{NeO}_3, \sim\text{NeO}_3$	192
<i>Terebencyl</i> : $\text{Te}=\text{3C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H}=\text{C}_{14}\text{H}_7$	193
Hydrate of terebenzinic acid: $\text{HO}, \text{TeO}_3$	193
PAIRED COMBINATIONS OF THE NICID GROUP AND THE NICYL GROUP	193
1. Pairling: $\text{C}_2\text{H}_2\text{O}_2$	193
a. <i>Furfural</i> : $\text{FuO}_2=\text{C}_2\text{H}_2\text{O}_2, \sim(\text{C}_2\text{H}_2, \text{C}_6\text{H})\text{O}_2=(\text{C}_{10}\text{H}_4\text{O}_2)\text{O}_2$	193
Sulpho-furfural: $\text{FuS}_2$	194
Nitro-furfural: $\text{Fu}_3\text{N}_2$	194
b. <i>Chinon</i> : $\text{ChoO}_2=\text{C}_2\text{H}_2\text{O}_2, \sim(\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_2=(\text{C}_{12}\text{H}_4\text{O}_2)\text{O}_2$	194
Colorless hydrochinon: $\text{ChoO}_2+\text{H}_2$	194
Green hydrochinon: $\text{ChoO}_2+\text{H}$	195
Hydrochlorate of hydrochinon: $\text{ChoO}_2+\text{HCl}$	195
Brown sulphohydrochinon: $\text{ChoO}_2+\text{S}+\text{HS}$	195
Yellow sulphohydrochinon: $\text{ChoO}_2+\text{H}+\text{HS}$	195
Rhombohedral sulphohydrochinon: $3(\text{ChoO}, \text{H})+2\text{HS}$	195
Derived radicals of chinon	196
Bichlorchinon: $\text{Cl}_2\text{ChoO}_2=\text{C}_2\text{H}_2\text{O}_2, \sim(\text{C}_2\text{Cl}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_2=(\text{C}_{12}\text{H}_2\text{Cl}_2\text{O}_2)\text{O}_2$	196
Trichlorchinon: $\text{Cl}_3\text{ChoO}_2=\text{C}_2\text{H}_2\text{O}_2, \sim(\text{C}_2\text{Cl}_2, \text{C}_6, \text{C}_2\text{Cl})\text{O}_2=(\text{C}_{12}\text{HCl}_3\text{O}_2)\text{O}_2$	196
Tetrachlorchinon (Chloranil): $\text{Cl}_4\text{ChoO}_2=\text{C}_2\text{Cl}_2\text{O}_2, \sim(\text{C}_2\text{Cl}_2, \text{C}_6, \text{C}_2\text{Cl})\text{O}_2=(\text{C}_{12}\text{Cl}_4\text{O}_2)\text{O}_2$	197
Hydrate of chloranilic acid: $\text{HO}(\text{C}_6\text{Cl})\text{O}_3$	197
Hydrate of chloranilamidic acid: $\text{HO}(\text{NH}_2, \text{C}_6\text{Cl})\text{O}_2, \sim(\text{C}_6\text{Cl})\text{O}_3$	198
2. Pairling: $\text{C}_4\text{H}_2$	198
a. Phenol (Spirol): $\text{HO}, \text{SprO}=\text{C}_4\text{H}_2, \sim(\text{C}_2\text{H}_2, \text{C}_6\text{H})\text{O}=\text{HO}, (\text{C}_{12}\text{H}_5)\text{O}$	199
Creosote: $\text{HO}, \text{CroO}=\text{C}_4\text{H}_2(2\text{C}_2\text{H}_2, \text{C}_6\text{H})\text{O}=\text{HO}(\text{C}_{14}\text{H}_7)\text{O}$	199
Guaiacol: $\text{HO}(\text{C}_{14}\text{H}_7)\text{O}_4(?)$	200
Carvacrol: $\text{HoCro}=\text{C}_4\text{H}_2, \sim(7\text{C}_2\text{H}_2, \text{C}_6\text{H})\text{O}=\text{HO}(\text{C}_{24}\text{H}_{17})\text{O}$	200
b. Phenolic acid: $\text{HO}, \text{PhnO}_3=\text{C}_4\text{H}_2, \sim(\text{C}_6, \text{C}_2\text{H})\text{O}_3=\text{HO}(\text{C}_{12}\text{H}_3)\text{O}_3$	201
Bichlorphenolic acid (Chlorphenessic A.): $\text{HO}, \text{PhnOCl}_2=\text{C}_4\text{H}_2, \sim(\text{C}_6, \text{C}_2\text{H})\text{OCl}_2=\text{HO}(\text{C}_{12}\text{H}_3)\text{OCl}_2$	201
Terechlorphenolic acid (Chlorphenissic A.): $\text{HO}, \text{ClPhnOCl}_2=\text{C}_4\text{H}_2, \sim(\text{C}_6, \text{C}_2\text{Cl})\text{OCl}_2=\text{HO}(\text{C}_{12}\text{H}_2\text{Cl})\text{OCl}_2$	201
Pentachlor-phenolic acid (Chlorphenussic A.): $\text{HO}, \text{Cl}_5\text{PhnOCl}_2=\text{C}_4\text{Cl}_2, \sim(\text{C}_6, \text{C}_2\text{Cl})\text{OCl}_2=\text{HO}(\text{C}_{12}\text{Cl}_3)\text{OCl}_2$	202
Bromphenolic acid (Bromphenissic A.): $\text{HO}, \text{BrPhnOBr}_2=\text{C}_4\text{H}_2, \sim(\text{C}_6, \text{C}_2\text{Br})\text{OBr}_2=\text{HO}(\text{C}_{12}\text{H}_2\text{Br})\text{OBr}_2$	202
Nitrophenolic acid (Nitrophenessic A.): $\text{HO}, \text{PhnOX}_2=\text{C}_4\text{H}_2, \sim(\text{C}_6, \text{C}_2\text{H})\text{OX}_2=\text{HO}(\text{C}_{12}\text{H}_3)\text{OX}_2$	202
Pikrin-nitric acid (Nitrophenissic): $\text{HO}, x\text{PhnOX}_2=\text{C}_4\text{H}_2, \sim(\text{C}_6, \text{C}_2\text{X})\text{OX}_2=\text{HO}(\text{C}_{12}\text{H}_2\text{X})\text{OX}_2$	202
Oxypikrin-nitric acid: $\text{HO}^x\text{PhnO}_3\text{X}_2=\text{C}_4\text{H}_2, \sim(\text{C}_6, \text{C}_2\text{XO}_3\text{X}_2=\text{HO}(\text{C}_{12}\text{H}_2\text{X})\text{O}_3\text{X}_2$	204
Pikranisic acid: $\text{HO}, (\text{C}_{12}\text{H}_2\text{X})\text{OX}_2$	205
3. Pairling: $\text{C}_4\text{H}_2\text{O}_2$	205
a. Anise oil: $\text{AoH}=\text{C}_4\text{H}_2\text{O}_2, \sim(2\text{C}_2\text{H}_2, \text{C}_6\text{H})\text{H}=(\text{C}_{14}\text{H}_7\text{O}_2)\text{H}$	205
Brom-anise oil: $\text{AoBr}$	205
Nitro-anise oil: $\text{AoX}$	205
Sulph-anise oil: $\text{AoSO}_2$	206
Phenetol: $\text{PhoH}=\text{C}_4\text{H}_2\text{O}_2, \sim(3\text{C}_2\text{H}_2, \text{C}_6\text{H})=(\text{C}_{16}\text{H}_9\text{O}_2)\text{H}$	206
Anise-camphor: $\text{C}_4\text{H}_2, \sim\text{PhoH}=(\text{C}_{20}\text{H}_{11}\text{O}_2)\text{H}$	206
Anisoin: $\text{C}_{40}\text{H}_{24}\text{O}_4$	206
b. <i>Salicyl</i> (Spiroyl): $\text{Sa}=\text{C}_4\text{H}_2\text{O}_2, \sim(\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})=(\text{C}_{14}\text{H}_5\text{O}_2)$	207
Salicylous acid: $\text{SaO}$	207
Hydrate of salicylous acid: $\text{HO}, \text{SaO}$	207



	PAGE
Derived radicals of salicyl	209
<i>Bichlorsalicyl</i> : $C_2Sa=C_4H_2.O_2\sim(C_2Cl_2.C_6.C_2H)=C_{14}H_3Cl_2O_2$	209
Hydrate of bichlorsalicylous acid: $HO,Cl_2SaO$	209
Salicylic acid: $SaO_3$	210
Hydrate of salicylic acid: $HO,SaO_3$	210
<i>Trichlorsalicyl</i> : $Cl_3Sa=C_4H_2.O_2\sim(C_2Cl_2.C_6.C_2Cl)=C_{14}H_2Cl_3O_2$	211
Hydrate of trichlorsalicylic acid: $HO,Cl_3SaO_3$	211
Tribromanisol: $SaBr_3$	212
Salicylnitrid: $SaX_3$	212
Hydrate of bichlorsalicylic acid: $HO,Cl_2SaO_3$	213
<i>Bibromsalicyl</i> : $Br_2Sa=C_4H_2.O_2\sim(C_2Br_2.C_6.C_2H)=C_{14}H_3Br_2O_2$	213
Hydrate of bibromsalicylous acid: $HO,Br_2SaO$	213
Hydrate of bibromsalicylic acid: $HO,Br_3SaO_3$	213
<i>Tribromsalicyl</i> : $Br_3Sa=C_4H_2.O_2\sim(C_2Br_2.C_6.C_2Br)=C_{14}H_2Br_3O_2$	213
Hydrate of tribrom-salicylic acid: $HO,Br_3SaO_3$	213
<i>Binitro-salicyl</i> : $x_2Sa=C_4H_2.O_2\sim(C_2X_2.C_6.C_2H)=C_{14}H_3X_2O_2$	213
Hydrate of binitro-salicylous acid: $HO,x_2SaO$	213
Hydrate of binitro-salicylic acid: $HO,x_3SaO_3$	213
<i>Trinitro-salicyl</i> : $x_3Sa=C_4H_2.O_2\sim(C_2X_2.C_6.C_2X)=C_{14}H_2X_3O_2$	214
Hydrate of trinitro-salicyl: $HO,x_3SaO_3$	214
PAIRED RADICAL OF SALICYL	214
<i>Coumaryl</i> : $Cou=C_4H_2\sim Sa=C_{15}H_7O_2$	214
Hydrate of coumarylous acid: $HO,CouO$	214
Hydrate of coumarylic acid: $HO,CouO_3$	215
Saligenin(?): $HO,C_4H_4O_2\sim(C_2H_2.C_6.C_2H)O$	215
<i>Anisyl</i> : $An=C_4H_2.O_2(2C_2H_2.C_6.C_2H)=C_{16}H_7O_2$	216
Anisylous acid: $AnO$	216
Hydrate of anisylous acid: $HO,AnO$	216
Anisyllic acid: $AnO_3$	216
Hydrate of anisyllic acid: $HO,AnO_3$	216
Bioxychloride of anisyl: $AnClO_3$	217
Bioxybromide of anisyl: $AnBrO_2$	217
Hydrate of bibromanisyllic acid: $HO,Br_2AnO_3$	217
Hydrate of binitro-anisyllic acid: $HO,x_2AnO_3$	218
<i>Salt-like Combinations of the Acids of Salicyl and Anisyl</i>	218
Salicylate of methyl: $MeO,SaO_3$	219
Bichlorsalicylate of methyl: $MeO,Cl_2SaO_3$	219
Binitro-salicylate of methyl: $MeO,x SaO_3$	219
Trinitro-salicylate of methyl: $MeO,x SaO_3$	219
Anisylate of methyl: $MeO,AnO_3$	219
Salicylate of ethyl: $AeO,SaO_3$	219
Anisylate of ethyl: $AeO,AnO_3$	219
APPENDIX TO THE ACIDS OF THIS GROUP	220
Caryophyllic acid: $HO,CryO_3=C_4H_2.O_2\sim(6C_2H_2.C_6.C_2H)O_3=HO,C_{24}H_{15}O_5$	220
Guaiac acid: $HO,GuO_3=C_2H_4.O_2\sim(C_2H_2.C_6.C_2H)O_3=HO,C_{12}H_7O_5$	220

## FOURTH GROUP.

*Carbon Nucleus: C<sub>6</sub>.*

1. <i>Benzid Group</i> . General formula: Component, $x C_2H_2$ ; Nucleus, $C_8$ ; Active part, H	220
<i>Benzid</i> : $Bd=2C_2H_2.C_8.H=C_{12}H_5$	220
Hydrobenzid: $BdH$	221
Chlorbenzid: $BdCl$	222
Azobenzid: $BdN$	222
Azoxybenzid: $BdO_2+BdN_2$	222



	PAGE
Sulpho-benzid: $\text{BdSO}_2$	223
Sulpho-benzid-sulphuric acid: $\text{HO}(\text{Bd}, \text{SO}_2) \sim \text{SO}_3$	223
PAIRED COMBINATIONS OF BENZID	223
1. <i>Picramyl</i> : $\text{Per}=\text{C}_2\text{H} \sim (2\text{C}_2\text{H}_2, \text{C}_8, \text{H})=\text{C}_{14}\text{H}_6$	223
Oxide of picramyl: $\text{PerO}_2$	224
Benzoin: $\text{C}_{23}\text{H}_{12}\text{O}_4$	224
Stilbyl: $\text{C}_{25}\text{H}_{11}\text{O}_4$	225
Benzil: $\text{C}_{23}\text{H}_{10}\text{O}_4$	225
Benzilic acid: $\text{HO}(\text{C}_{23}\text{H}_{11})\text{O}_5$	225
Sulphide of picramyl: $\text{PerS}_2$	226
Thionessal: $\text{C}_{26}\text{H}_9\text{S}$	226
Protochloride of picramyl: $\text{PerCl}$	226
Bichloride: $\text{PerCl}_2$	226
Protochloride of stilbyl: $\text{C}_{12}\text{H}_{11}\text{Cl}$	226
Protobromide of picramyl: $\text{PerBr}$	227
Nitro-picramyl: $\text{Per}_3\text{N}_2$	227
Benzostilbin: $\text{C}_{16}\text{H}_6\text{O}$	227
Benzolon: $\text{C}_{22}\text{H}_8\text{O}_2$	227
Picramyloxyd-sulphuric acid: $\text{HO}, \text{PerO}_2, \sim \text{SO}_3(?)$	228
Picramyloxyd-formic acid: $\text{HO}, \text{PerO}_2, \sim \text{FoO}_3$	228
Benziminic acid	228
PAIRED RADICALS OF PICRAMYL	228
<i>Cinnamyl</i> : $\text{Cy}=\text{C}_4\text{H}_2 \sim (\text{C}_{14}\text{H}_6)=\text{C}_{18}\text{H}_8$	228
Oxide of cinnamyl: $\text{CyO}_2$	228
Sulphide of cinnamyl: $\text{CyS}_2$	229
Nitro-cinnamyl: $\text{Cy}_3\text{N}_2$	229
Oxychloride of chlorcinnamyl: $\text{Cl}_4\text{CyO}_2=(\text{C}_{18}\text{H}_4\text{Cl}_4)\text{O}_2$	229
Cinnamon oil: $\text{C}_2\text{H}_3 \sim (\text{C}_{18}\text{H}_8\text{O}_2)=\text{C}_{22}\text{H}_{11}\text{O}_2$	229
Cinnamein: $\text{C}_{36}\text{H}_{16}\text{O}_4$	229
Metacinnamein: $\text{C}_{36}\text{H}_{16}\text{O}_4$	230
Peruvín: $\text{C}_{18}\text{H}_{12}\text{O}_2$	230
Styron: $\text{C}_{18}\text{H}_{10}\text{O}_2$	230
2. <i>Cinnamid</i> : $\text{Cd}=\text{C}_4\text{H}_2 \sim (2\text{C}_2\text{H}_2, \text{C}_8, \text{H})=\text{C}_{16}\text{H}_7$	230
Hydro-cinnamid: $\text{CdH}$	230
Bromecinnamin: $\text{CdBr}$	231
Hydrobromate of bromecinnamin: $\text{CdBr} + \text{HBr}$	231
Nitrocinnamin: $\text{CdX}$	231
3. <i>Naphthalid</i> : $\text{Na}=\text{C}_8\text{H}_2 \sim (2\text{C}_2\text{H}_2, \text{C}_8, \text{H})=\text{C}_{20}\text{H}_7$	231
Hydonaphthalid: $\text{NaH}$	231
Oxide of naphthalid: $\text{NaO}$	232
Chloride of naphthalid: $\text{NaCl}$	232
Hydrochlorate of chloride of naphthalid: $\text{NaCl} + \text{HCl}$	232
Bromide of naphthalid: $\text{NaBr}$	232
Hydrobromate of bromide of naphthalid: $\text{NaBr} + \text{HBr}$	232
Nitronaphthalid: $\text{NaX}$	232
Sulphonaphthalid: $\text{NaSO}_2$	232
Sulphonaphthalid-sulphuric acid: $\text{HO}, (\text{NaSO}_2) \sim \text{SO}_3$	233
4. <i>Anthracid</i> : $\text{Anr}=\text{C}_{18}\text{H}_6 \sim (2\text{C}_2\text{H}_2, \text{C}_8, \text{H})=\text{C}_{30}\text{H}_{11}$	233
Hydroanthracid: $\text{AnrH}$	233
Nitroanthracid: $\text{AnrX}$	234
Pyren: $\text{C}_{30}\text{H}_{12}$	234
5. <i>Chrysid</i> : $\text{Chr}=\text{C}_{30}\text{H}_8 \sim (2\text{C}_2\text{H}_2, \text{C}_8, \text{H})=\text{C}_{42}\text{H}_{13}$	234
Hydrochrysid: $\text{ChrH}$	234
Idryl: $\text{C}_{42}\text{H}_{14}$	234
Idrialin: $\text{C}_{42}\text{H}_{14}\text{O}$	235
Retisterin: $\text{C}_{20}\text{H}_8 \sim (2\text{C}_2\text{H}_2, \text{C}_8, \text{H})\text{H}=\text{C}_{32}\text{H}_{14}$	235
Ritinol: $\text{C}_{32}\text{H}_{16}$	235
Hydrocarbons: $=\text{C}_{16}\text{H}_{16}$ ; $\text{C}_{20}\text{H}_{16}$ ; $\text{C}_{24}\text{H}_{16}$ ; $\text{C}_{28}\text{H}_{16}$	235
Eupion	235

	PAGE
Ampelin . . . . .	236
<i>Tolid</i> : $Td=3C_2H_2.C_8.H=C_{14}H_7$ . . . . .	236
Hydrotolid: $TdH$ . . . . .	236
Chloride of tolid: $TdCl$ . . . . .	236
Nitrotolid: $TdX$ . . . . .	236
Sulphotolid: $TdSO_2$ . . . . .	237
Sulphotolid-sulphuric acid: $HO.(Td,SO_2).SO_3$ . . . . .	237
<i>Xyloid</i> : $Xd=4C_2H_2.C_8.H=C_{16}H_9$ . . . . .	237
Hydroxyloid: $XdH$ . . . . .	237
<i>Cumid</i> : $Cd=5C_2H_2.C_8.H=C_{18}H_{11}$ . . . . .	237
Hydrocumid: $CdH$ . . . . .	237
Retinyl: $C_{18}H_{12}$ . . . . .	237
Mesitol: $C_{16}H_{12}$ . . . . .	238
Trinitro-mesitol: $(C_{18}H_9)X_3$ . . . . .	238
Trichlor-mesitol: $(C_{18}H_9)Cl_3$ . . . . .	238
Tribro-mesitol: $(C_{18}H_9)Br_3$ . . . . .	238
PAIRED RADICAL OF CUMID . . . . .	238
<i>Cumyl</i> : $Cu=C_2H.(5C_2H_2.C_8.H)=C_{20}H_{12}$ . . . . .	238
Oxide of cumyl: $CuO_2$ . . . . .	238
Chloride of cumyl: $CuCl_2$ . . . . .	239
<i>Cymid</i> : $Cy=6C_2H_2.C_8.H=C_{20}H_{13}$ . . . . .	239
Hydrocymid: $CyH$ . . . . .	239
<i>Tolen</i> : $To=8C_2H_2.C_8.H=C_{24}H_{18}$ . . . . .	239
2. <i>Benzoyl Group</i> . General formula: Component, $x C_2H_2$ ; Nucleus, $C_8$ ; Active part, $C_2H$ . . . . .	239
<i>Benzyl</i> : $Be=C_2H_2.C_8.C_2H=C_{12}H_3$ . . . . .	240
Chloride of benzyl: $BeCl_3$ . . . . .	240
Hydrochlorate of chloride of benzyl: $BeCl_3+3HCl$ . . . . .	241
Benzylnitrid: $BeX_3$ . . . . .	241
PAIRED COMBINATIONS OF BENZYL . . . . .	241
<i>Naphtyl</i> : $Ny=C_8H_2.(C_2H_2.C_8.C_2H)=C_{20}H_5$ . . . . .	241
Chloride of naphtyl: $NyCl_2$ . . . . .	241
Chloride of naphtyl-naphtalid: $NyCl_3+NaCl=C_{20}H_6Cl_2$ . . . . .	241
Hydrochlorate of proto- and ter-chloride of naphthalid: $NyCl_3, 3HCl_3$ + $NaCl, HCl$ . . . . .	241
Terchloride of bichlornaphtyl: $ClNyCl_3$ . . . . .	242
Naphtylnitrid: $NyX_3$ . . . . .	242
Naphtylsulpho-sulphuric acid: $3HO.(Ny, 3SO_2).3SO_3$ . . . . .	242
<i>Benzoyl</i> : $Bz=2C_2H_2.C_8.C_2H=C_{14}H_5$ . . . . .	243
Oxide of benzoyl: $BzO_2$ . . . . .	243
Benzoic acid: $BzO_3$ . . . . .	243
Hydrate of benzoic acid: $Ho, BzO_3$ . . . . .	243
Bioxy sulphide of benzoyl: $BzSO_2$ . . . . .	245
Chloride of benzoyl: $BzCl_3$ . . . . .	245
Bioxychloride of benzoyl: $BzClO_2$ . . . . .	245
Bioxybromide of benzoyl: $BzBrO_2$ . . . . .	245
Bioxydiodide of benzoyl: $BzIO_2$ . . . . .	245
Acetylchlorate of bioxychloride of benzoyl: $BzO_2Cl+AcOCl_2$ . . . . .	245
Benzoylnitrid: $BzX_3$ . . . . .	246
Nitrobenzoyl: $BzN$ . . . . .	246
Derived radicals of benzoyl.	
2. <i>Bichlorbenzoyl</i> : $Cl_2Bz=C_2H_2.C_2Cl_2.C_8.C_2H=C_{14}H_3Cl_2$ . . . . .	246
Bichlorbenzoic acid: $HO, Cl_2BzO_3$ . . . . .	246
3. <i>Tetrachlor-benzoyl</i> : $Cl_4Bz=2C_2Cl_2.C_8.C_2H=C_{14}HCl_4$ . . . . .	246
Tetrachlor-benzoic acid: $HO, Cl_4BzO_3$ . . . . .	246
Hydrochlorate of chloride of bichlorbenzoyl: $Cl_2BzCl_3, 2HCl$ . . . . .	246
4. <i>Binitrobenzoyl</i> : $Bz=xC_2H_2.C_2X_2.C_8.C_2H=C_{14}H_3X_2$ . . . . .	246
Binitrobenzoic acid: $HO, xBzO_3$ . . . . .	246
Bioxychloride of nitrobenzoyl: $xBzOCl_2$ . . . . .	247

Benzaminic acid: $\text{HO} \cdot (\text{C}_{14}\text{H}_4 \cdot \text{NH}_2) \text{O}_3$	247
Sulphobenzo-sulphuric acid: $2\text{HO}(\text{C}_{14}\text{H}_4 \cdot \text{SO}_2) \cdot \text{SO}_3$	248
PAIRED COMBINATIONS OF BENZOYL	248
<i>Cinnyl</i> : $\text{Cn} = \text{C}_4\text{H}_2 \cdot (2\text{C}_2\text{H}_2 \cdot \text{C}_8 \cdot \text{C}_2\text{H}) = \text{C}_{18}\text{H}_7$	248
Cinnamic acid: $\text{HO} \cdot \text{CnO}_3$	248
Bioxychloride of cinnyl: $\text{CnClO}_2$	249
Binitrocinnamic acid: $\text{HO} \cdot \text{CnO}_3$	249
Sulphocinnsulphuric acid: $2\text{HO}(\text{C}_{18}\text{H}_6 \cdot \text{SO}_2) \text{O}_3 \cdot \text{SO}_3$	249
Myroxyllic acid: $\text{HO} \cdot \text{C}_{15}\text{H}_6 \text{O}_3$	249
<i>Radicals of hippuric acid</i> : $\text{NC}_4\text{H}_3 \text{O}_2 \cdot (\text{C}_{11}\text{H}_5) = \text{NC}_{18}\text{H}_8 \text{O}_2$	249
Hydrate of hippuric acid: $\text{HO} \cdot (\text{NC}_{18}\text{H}_8 \text{O}_2) \text{O}_3$	249
<i>Benzon</i> : $\text{Bd} \cdot \text{BzO}_2 = \text{C}_{26}\text{H}_{10} \text{O}_2$	250
<i>Toluyll</i> : $\text{To} = 3\text{C}_2\text{H}_2 \cdot \text{C}_8 \cdot \text{C}_2\text{H} = \text{C}_{16}\text{H}_7$	251
Toluylic acid: $\text{ToO}_3$	251
Hydrate of toluylic acid: $\text{HO} \cdot \text{ToO}_3$	251
Nitrotoluylic acid: $\text{HO} \cdot \text{x}_2\text{ToO}_3$	251
<i>Cuminyll</i> : $\text{Cy} = 5\text{C}_2\text{H}_2 \cdot \text{C}_8 \cdot \text{C}_2\text{H} = \text{C}_{20}\text{H}_{11}$	251
Cuminylic acid: $\text{CyO}_3$	251
Hydrate of cuminylic acid: $\text{HO} \cdot \text{CyO}_3$	251
Bioxychloride of cuminyll: $\text{CyClO}_2$	252
Binitro-cuminic acid: $\text{HO} \cdot \text{x}_2\text{CyO}_3$	252

*Salt-like Combinations of the Oxides of the Methyl Group with the Acids of the Benzoyl Group.*

Benzoate of methyl: $\text{MeO} \cdot \text{BzO}_3$	252
Benzoate of ethyl: $\text{AeO} \cdot \text{BzO}_3$	252
Nitrobenzoate of ethyl: $\text{AeO} \cdot \text{x}_2\text{BzO}_3$	252
Cinnamate of ethyl: $\text{AeO} \cdot \text{CnO}_3$	252
Hippurate of ethyl: $\text{AeO} \cdot \text{NC}_{18}\text{H}_8 \text{O}_3$	252
Toluylate of ethyl: $\text{AeO} \cdot \text{ToO}_3$	253
Cuminate of ethyl: $\text{AeO} \cdot \text{CyO}_3$	253

APPENDIX TO THE ACIDS OF THESE GROUPS.

Carbon nucleus: $\text{C}_{10}(?)$	253
Aloetinic acid: $=\text{HO} \cdot (\text{C}_2\text{H}_2 \cdot \text{C}_2\text{X} \cdot \text{C}_{10} \cdot \text{C}_2\text{H}) \text{O}_4 = \text{C}_{16}\text{H}_4\text{N}_2\text{O}_{18}(?)$	253
Chrysamminic acid: $=\text{HO} \cdot (\text{C}_2\text{N}_2 \cdot \text{C}_{10} \cdot \text{C}_2\text{H}) \text{O}_3 = \text{HO} \cdot \text{C}_{14}\text{NH}_2\text{O}_{11}(?)$	253
Aloeresinic acid: $\text{C}_{12}\text{H}_4\text{N}_2\text{O}_9$	254
Hydrochrysamid: $\text{C}_{14}\text{H}_6\text{N}_2\text{O}_6$	254
Chrysaminamid: $\text{C}_{28}\text{H}_{10}\text{N}_7\text{O}_{24}$	254
Amido-chrysamminic acid: $\text{C}_{28}\text{H}_8\text{N}_6\text{O}_{22}$	254

FIFTH GROUP.

1. *Etheric Oils and Camphors.*

<i>Terebene or Camphene</i> : General formula $\text{xC}_{10}\text{H}_8$	256
Oil of turpentine: $2\text{C}_{10}\text{H}_8 = \text{C}_{20}\text{H}_{16}$	258
Terpinol: $\text{C}_{20}\text{H}_{16} \cdot \text{HO} = \text{C}_{20}\text{H}_{17} \text{O}$	259
Terpin: $\text{C}_{20}\text{H}_{16} \cdot 4\text{HO} = \text{C}_{20}\text{H}_{17} \text{O} + 3\text{HO}$	259
Hydrochlorate of oil of turpentine: $\text{C}_{20}\text{H}_{16} \cdot \text{HCl} = \text{C}_{20}\text{H}_{17} \cdot \text{Cl}$	259
Hydrobromate of oil of turpentine: $\text{C}_{20}\text{H}_{16} \cdot \text{HBr} = \text{C}_{20}\text{H}_{17} \cdot \text{Br}$	259
Hydriodate of oil of turpentine: $\text{C}_{20}\text{H}_{16} \cdot \text{HI} = \text{C}_{20}\text{H}_{17} \cdot \text{I}$	259
Tereben, camphilen, terebilen: $\text{C}_{20}\text{H}_{16}$	260
Chlorcamphen, chlortereben: $\text{C}_{20}\text{H}_{12}\text{Cl}_4$	260
Chlorturpentin: $\text{C}_{20}\text{H}_{12}\text{Cl}_4$	260
Colophen (Colophon): $=4\text{C}_{10}\text{H}_8 = \text{C}_{40}\text{H}_{32}$	260
Borneo camphor: $\text{C}_{10}\text{H}_9 \cdot \text{O} = \text{C}_{20}\text{H}_{18} \text{O}_2$	261
Laurus camphor: $\text{C}_{10}\text{H}_9 \cdot \text{O} = \text{C}_{20}\text{H}_{16} \text{O}_2$	261
Lemon oil, bergamot, orange, and copaiva oil: $=\text{C}_{20}\text{H}_{16}$	263
Caoutchun: $\text{C}_{20}\text{H}_{16}$	264
Petrolen and oil of wine: $\text{C}_{20}\text{H}_{16}$	264
<i>Oils which do not belong to class Terebenes</i>	265
Valerol: $\text{C}_{12}\text{H}_{10} \text{O}_2$ . Sage oil: $\text{C}_{12}\text{H}_{10} \text{O}$	265

	PAGE
Wormseed oil: $C_{18}H_{15}O_2$ Cedar oil: $C_{32}H_{26}$ . . . . .	265
Cedar camphor: $C_{32}H_{28}O_2$ . . . . .	265
Menthen: $C_{20}H_{18}$ Menthen camphor: $C_{20}H_{20}O_2$ . . . . .	265
Monarda oil: $C_{30}H_{21}O$ . . . . .	266
Monarda camphor: $C_{20}H_{14}O_2$ . . . . .	266
Nutmeg-flower camphor: $C_{16}H_{16}O_5$ . . . . .	266
Marjorana camphor: $C_{14}H_{15}O_5$ . . . . .	266
Sassafras camphor: $C_{20}H_{10}O_4$ . . . . .	266
Violet camphor . . . . .	266
Helenium camphor: $C_{21}H_{14}O_3$ . . . . .	266
Asarum camphor: $C_{20}H_{13}O_5$ . . . . .	267
Anemone camphor: $C_{15}H_6O_6$ . . . . .	267
Cantharides camphor: $C_{10}H_6O_4$ . . . . .	267
<i>Ferment oils</i> . . . . .	268
2. <i>Resins.</i>	
<i>Resins corresponding to the terebenes</i> . . . . .	270
Silvic, pinic, and pimaric acid: $HO, C_{40}H_{29}O_3$ . . . . .	270
Dammaric acid: $HO, C_{40}H_{29}O_7$ . . . . .	271
Copaivic acid: $HO, C_{40}H_{29}O_3$ . . . . .	271
Resin of Peru balsam: $HO, C_{40}H_{27}O_5$ . . . . .	272
Sandarach . . . . .	272
Olibanum, mastich, copal, amber . . . . .	273
Asphalt, etc. . . . .	274
Gum-lac, benzoin resin, guaiac resin . . . . .	274
Resin of xanthorrhoea hastilis, etc. . . . .	275
<i>Gum resins</i> . . . . .	275
Ammonia gum, galbanum, sagapenum, assafetida, opoponax, myrrh, etc. . . . .	275
Caoutchouc, gutta-percha, viscina . . . . .	276
APPENDIX TO THE RESINS . . . . .	277
Lichenstearic acid: $HO, C_{28}H_{23}O_5$ . . . . .	277
Anacardic acid: $2HO, C_{44}H_{30}O_5$ . . . . .	277
Anacardium oil: $C_{42}H_{31}O_4$ . . . . .	278
Lithofellinic acid: $HO, C_{40}H_{36}O_7$ . . . . .	278
Cholalic acid: $HO, C_{48}H_{39}O_9$ . . . . .	278
Choloidic acid: $HO, C_{48}H_{39}O_9$ . . . . .	279
Dyslysin: $C_{48}H_{36}O_6$ . . . . .	279
Nitracol, cholacrol: $C_8H_5X_2O_5$ . . . . .	279
Cholesterin: $2HO, C_{81}H_{69}O_3$ . . . . .	279
Cholesterilens: $C_{32}H_{26}$ ; $C_{22}H_{18}$ ; $C_{27}H_{22}$ . . . . .	280
Cholesteric acid: $C_8H_4O_4$ . . . . .	280
Ambrain: $C_{26}H_{33}O$ . . . . .	280
Castorin, cerebrie acid . . . . .	280
II. CARBYLS.	
<i>Oxalic acid</i> : $OxO_3=C_2O_3=HO, OxO_3$ . . . . .	281
Oxalate of methyl: $MeO, OxO_3$ . . . . .	283
Oxalate of ethyl: $AeO, OxO_3$ . . . . .	283
Oxamid-oxalic acid: $HO, (NH_2, OxO_2) \sim OxO_3$ . . . . .	283
Ether-oxalic acid: $HO, (AeO, OxO_2) \sim OxO_3$ . . . . .	283
Oxalate of bichloroxide of chloracetyl: $(C_4Cl_3)Cl_2O + OxO_3$ . . . . .	284
Chloracetyl-bichloroxyd-oxalic acid: $HO[(C_4Cl_3)Cl_2O, OxO_3] \sim OxO_3$ . . . . .	284
Chloroxalamid: $[(C_4Cl_3)Cl_2O + OxO_3] + NH_2, OxO_3$ . . . . .	284
PAIRED COMPOUNDS OF OXALIC ACID . . . . .	285
Fumaric acid: $HO, C_4H_4O_3$ . . . . .	286
Parafumaric acid: $C_4H_4O_3$ . . . . .	286
Aconitic acid: $HO, C_4H_4O_3$ . . . . .	287
Malic acid: $HO, C_4H_2O_4=2HO, C_8H_4O_3$ . . . . .	287

	PAGE
Malamid, malaminic acid . . . . .	289
Tartaric acid: $\text{HO}, \text{C}_4\text{H}_2\text{O}_5 = 2\text{HO}, \text{C}_8\text{H}_4\text{O}_{10}$ . . . . .	289
Antitartaric acid: $\text{HO}, \text{C}_4\text{H}_2\text{O}_5$ . . . . .	293
Racemic acid: $\text{HO}, \text{C}_4\text{H}_2\text{O}_5$ . . . . .	293
Itaconic acid: $\text{HO}, \text{C}_5\text{H}_2\text{O}_3$ . . . . .	294
Citraconic acid: $\text{HO}, \text{C}_5\text{H}_2\text{O}_3$ . . . . .	295
Pyrotartaric acid: $\text{HO}, \text{C}_5\text{H}_3\text{O}_3$ . . . . .	296
Pyroracemic acid: $\text{HO}, \text{C}_6\text{H}_3\text{O}_5$ . . . . .	296
Citric acid: $\text{HO}, \text{C}_6\text{H}_3\text{O}_6$ . . . . .	297
Saccharic acid: $\text{HO}, \text{C}_6\text{H}_4\text{O}_7$ . . . . .	298
Mucic acid: $\text{HO}, \text{C}_6\text{H}_4\text{O}_7$ . . . . .	299
Chelidonic acid: $\text{HO}, \text{C}_7\text{H}_5\text{O}_5$ . . . . .	300
Meconic acid: $\text{HO}, \text{C}_7\text{H}_5\text{O}_6$ . . . . .	301
Komenic acid: $\text{HO}, \text{C}_7\text{H}_5\text{O}_4$ . . . . .	302
Pyromucic acid: $\text{HO}, \text{C}_{10}\text{H}_3\text{O}_5$ . . . . .	302
Pyromeconic acid: $\text{HO}, \text{C}_{10}\text{H}_3\text{O}_5$ . . . . .	303
Kinic acid: $\text{HO}, \text{C}_{14}\text{H}_{10}\text{O}_{10}$ . . . . .	303
Veratric acid: $\text{HO}, \text{C}_{18}\text{H}_9\text{O}_7$ . . . . .	304
Opianic acid: $\text{HO}, \text{C}_{20}\text{H}_9\text{O}_9$ . . . . .	304
Mesoxalic acid: $\text{HO}, \text{C}_3\text{O}_4 = 2\text{HO}, \text{C}_6\text{O}_8$ . . . . .	306
Mellitic acid: $\text{HO}, \text{C}_4\text{O}_3$ . . . . .	306
Paramid: $\text{HO}, (\text{NC}_1)\text{C}_4\text{O}_3$ . . . . .	307
Paramidic acid: $2\text{HO}, (3\text{NH}, \text{C}_4\text{O}_2), \sim 3\text{C}_4\text{O}_3$ . . . . .	307
Euchronic acid: $2\text{HO}, (\text{NC}_4)2\text{C}_4\text{O}_3 + 2\text{aq}$ . . . . .	307
Croconic acid: $\text{HO}, \text{C}_5\text{O}_4$ . . . . .	308
Rhodizonic acid . . . . .	308

## III. AZOCARBYLS.

<i>Cyanogen</i> : $\text{Cy}=\text{NC}_2$ . . . . .	310
Hydrocyanic acid: $\text{HCy}$ . . . . .	312
Cyanides of metals . . . . .	313
Simple cyanides of metals: $\text{MCy}$ , and $\text{M}_2\text{Cy}_3$ . . . . .	315
Double cyanides . . . . .	317
Cyanide of potassium-manganese: $\text{K}_3+(\text{Mn}_2\text{Cy}_3)\text{Cy}_3$ . . . . .	317
Hydroferrocyanic acid: $\text{H}_2+(\text{FeCy})\text{Cy}_2$ . . . . .	317
Ferrocyanide of metals: $\text{M}_2+(\text{FeCy})\text{Cy}_2$ . . . . .	317
Hydroferricyanic acid: $\text{H}_3(\text{Fe}_2\text{Cy}_3)\text{Cy}_3$ . . . . .	319
Ferricyanide of metals: $\text{M}_3(\text{Fe}_2\text{Cy}_3)\text{Cy}_3$ . . . . .	319

## NITROFERROCYNANOGEN COMPOUNDS.

Nitroferriecyanhydric acid: $\text{H}_2+(\text{Fe}_2\text{Cy}_3\text{NO}_2)\text{Cy}_2$ . . . . .	321
Ferricyanides of metals: $\text{M}_2+(\text{Fe}_2\text{Cy}_3\text{NO}_2)\text{Cy}_2$ . . . . .	321
Hydrochromcyanic acid: $\text{H}_3+(\text{Cr}_2\text{Cy}_3)\text{Cy}_3$ . . . . .	322
Chromcyanides of metals: $\text{M}_3+(\text{Cr}_2\text{Cy}_3)\text{Cy}_3$ . . . . .	322
Hydrocobaltcyanic acid: $\text{H}_3+(\text{Co}_2\text{Cy}_3)\text{Cy}_3$ . . . . .	322
Nickelcyanides of metals: $\text{M}+(\text{NiCy})\text{Cy}$ . . . . .	322
Mercurycyanide of metals: $\text{M}+(\text{HgCy})\text{Cy}$ . . . . .	322
Hydrosilvercyanic acid: $\text{H}+(\text{AgCy})\text{Cy}$ . . . . .	322
Silvercyanides of metals: $\text{M}+(\text{AgCy})\text{Cy}$ . . . . .	322
Hydroplatinocyanic acid: $\text{H}+(\text{PtCy})\text{Cy}$ . . . . .	322
Platinumcyanide of metals: $\text{M}+(\text{PtCy})\text{Cy}$ . . . . .	322
Aurocyanide of metals: $\text{M}+(\text{AuCy})\text{Cy}$ . . . . .	322
Auricyanide of metals: $\text{M}+(\text{AuCy}_3)\text{Cy}$ . . . . .	323
Cyanic acid: $\text{CyO}$ . . . . .	323
Hydrate of cyanic acid: $\text{HO}, \text{CyO}$ . . . . .	324
Cyanate of methyl: $\text{MeO}, \text{CyO}$ . . . . .	325
Cyanate of ethyl: $\text{AeO}, \text{CyO}$ . . . . .	325
Cyanate of amyl: $\text{AmO}, \text{CyO}$ . . . . .	325
Sulphide of cyanogen: $(\text{CyS})\text{S}$ . . . . .	325
Hydrosulphocyanic acid: $\text{H}+(\text{CyS})\text{S}$ . . . . .	325
Sulphocyanides of metals: $\text{M}+(\text{CyS})\text{S}$ . . . . .	326



	PAGE
Sulphocyanide of methyl: $\text{Me}(\text{CyS})\text{S}$ . . . . .	327
Sulphocyanide of ethyl: $\text{Ae}+(\text{CyS})\text{S}$ . . . . .	327
Sulphocyanide of allyl: $\text{All}+(\text{CyS})\text{S}$ . . . . .	327
Bisulphocyanogen: $(\text{CyS}_2)\text{S}$ . . . . .	327
Hydrobisulphocyanic acid: $\text{H}+(\text{CyS}_2)\text{S}$ . . . . .	328
Hydrobisulphocyanide of metals: $\text{M}+(\text{CyS}_2)\text{S}$ . . . . .	328
Cyanide of selenium: $(\text{CySe})\text{S}$ . . . . .	328
Protochloride of cyanogen: $\text{CyCl}$ . . . . .	328
Metachloride of cyanogen: $\text{N}_3\text{C}_6\text{Cl}_3$ . . . . .	329
Bichloride of cyanogen: $\text{CyCl}_2$ . . . . .	329
Bromide of cyanogen: $\text{CyBr}$ . . . . .	329
Iodide of cyanogen: $\text{CyI}$ . . . . .	329
<i>Paraban</i> : $\text{PrN}_2\text{C}_6$ . . . . .	330
Hydrate of parabanic acid: $2\text{HO}, \text{PrO}_4$ . . . . .	330
<i>Fulminan</i> : $\text{Fu}=\text{N}_2\text{C}_4$ . . . . .	330
Fulminate of metals: $(\text{MFu})\text{O}_3$ . . . . .	330
Zinc-fulminic acid: $\text{HO}, (\text{ZnFu})\text{O}_3$ . . . . .	331
Copper-fulminic acid: $\text{HO}, (\text{CuFu})\text{O}_3$ . . . . .	331
Mercury-fulminic acid: $\text{HO}, (\text{Hg}_2\text{Fu})\text{O}_3$ . . . . .	331
Mercury-fulminate of protoxide of mercury: $\text{Hg}_2\text{O}, (\text{Hg}_2\text{Fu})\text{O}_3$ . . . . .	331
Silver-fulminic acid: $\text{HO}, (\text{AgFu})\text{O}_3$ . . . . .	331
Silver-fulminate of silver: $\text{AgO}, (\text{AgFu})\text{O}_3$ . . . . .	331
<i>Mellan</i> : $\text{Mll}=\text{N}_4\text{C}_6$ . . . . .	332
Hydromellanic acid: $\text{HMLl}$ . . . . .	332
Sulpho-mellan: $\text{MllS}$ . . . . .	333

## IV. HYDROAZOCARBYLS.

<i>Uren</i> : $\text{Ur}=\text{NC}_2\text{H}$ . . . . .	334
Oxide of uren: $\text{UrO}_2$ . . . . .	334
Hydrosulphbiurenic acid: $\text{H}+(\text{Ur}_2\text{S})\text{S}$ . . . . .	335
Hydrosulphurenic acid: $\text{H}+(\text{UrS})\text{S}$ . . . . .	335
Hydrobisulphurenic acid: $\text{H}+(\text{UrS}_2)\text{S}$ . . . . .	335
Hydrotrisulphurenic acid: $\text{H}+(\text{UrS}_3)\text{S}$ . . . . .	335
So-called sulphide of cyanogen: $\text{N}_2\text{C}_4\text{H}_2\text{S}_4\text{O}$ . . . . .	336
Thiocyanhydric acid: $\text{N}_5\text{C}_{10}\text{H}_6\text{S}_{12}\text{O}_3$ . . . . .	336
Cyanurenic acid: $2\text{HO}+(\text{UrO}_2)\text{S}_2\text{CyO}$ . . . . .	336
Mellanurenic acid: $\text{N}_4\text{C}_6\text{H}_4\text{O}_4$ . . . . .	337
Allophanic acid: $\text{HO}(\text{UrO}_2, \text{NH}_2)\text{OxO}_3=\text{HO}, \text{N}_2\text{C}_4\text{H}_3\text{O}_5$ . . . . .	337
Trigenic acid: $\text{HO}, (\text{Ur}_3)\text{C}_2\text{H}_2\text{O}_3=\text{HO}, \text{N}_3\text{C}_5\text{H}_5\text{O}_3$ . . . . .	338
Uric acid: $2\text{HO}+(\text{Ur}, \text{NH}), \text{N}_2\text{C}_8\text{O}_4$ . . . . .	338
Allantoin: $\text{HO}, \text{N}_4\text{C}_8\text{H}_5\text{O}_5$ . . . . .	340
Alloxan: $2\text{HO}, \text{N}_2\text{C}_8\text{H}_2\text{O}_8$ . . . . .	340
Alloxantin: $2\text{HO}, \text{N}_2\text{C}_8\text{H}_3\text{O}_8$ . . . . .	341
Alloxanic acid: $\text{HO}, \text{NC}, \text{HO}$ . . . . .	341
Thionuric acid: $2\text{HO}, (\text{N}_3\text{C}_8\text{H}_5\text{O}_6)\text{S}_2\text{SO}_3$ . . . . .	342
Uramil: $\text{N}_3\text{C}_8\text{H}_2\text{O}_6$ . . . . .	342
Uramilic acid: $\text{N}_5\text{C}_{16}\text{H}_{10}\text{O}_5$ . . . . .	342
Murexyd: $\text{N}_{10}\text{C}_{24}\text{H}_{12}\text{O}_{16}$ . . . . .	342
Murexan: $\text{N}_4\text{C}_{12}\text{H}_8\text{O}_{10}$ . . . . .	343
Amelinic acid: $(2\text{C}_2\text{H}_2), \text{N}_2\text{C}_6\text{H}_3\text{O}_8$ . . . . .	344
Murexoin: $(6\text{C}_2\text{H}_2), \text{N}_{10}\text{C}_{24}\text{H}_{11}\text{O}_{15}$ . . . . .	344
Cholestrophan: $(2\text{C}_2\text{H}_2), \text{N}_2\text{C}_8\text{H}_2\text{O}_6$ . . . . .	344
Oxaluric acid: $\text{HO}, \text{N}_2\text{C}_6\text{H}_3\text{O}_7$ . . . . .	344
Dialuric acid: $\text{HO}, \text{N}_2\text{C}_8\text{H}_3\text{O}_7$ . . . . .	344
Mykomelinic acid: $\text{N}_4\text{C}_8\text{H}_5\text{O}_5$ . . . . .	345
Allanturic acid: $\text{N}_4\text{C}_{10}\text{H}_7\text{O}_9$ . . . . .	345
Hydurilic acid: $2\text{HO}, \text{N}_3\text{C}_{10}\text{H}_3\text{O}_9$ . . . . .	345
Allituric acid: $\text{HO}, \text{N}_2\text{C}_6\text{H}_2\text{O}_3$ . . . . .	345
Dilituric acid: $2\text{HO}, \text{N}_3\text{C}_6\text{H}_3\text{O}_8$ . . . . .	345
Leucoturic acid: $\text{N}_2\text{C}_6\text{H}_3\text{O}_6$ . . . . .	345
Difluan: $\text{N}_2\text{C}_6\text{H}_5\text{O}_5$ . . . . .	345
Hidantoinic acid: $\text{HO}, \text{N}_4\text{C}_8\text{H}_8\text{O}_8$ . . . . .	346



Hyperuric acid: $2\text{HO}, \text{N}_4\text{C}_{10}\text{H}_7\text{O}_3$	346
Xanthic-oxyd: $\text{N}_2\text{C}_5\text{H}_2\text{O}_2$	346
Rosaic acid	346

ORGANIC ALKALIDS.

Glycocoll: $(\text{NH}_2, \text{C}_2\text{H}_2\text{O}_2) \text{C}_2\text{H}_2\text{O}_2 = \text{NC}_4\text{H}_5\text{O}_4$	347
Alanin: $(\text{NH}_2, \text{C}_4\text{H}_4\text{O}_2) \text{C}_2\text{H}_2\text{O}_2 = \text{NC}_6\text{H}_7\text{O}_4$	348
Sarkosin: $\text{NC}_6\text{H}_7\text{O}_4$	348
Leucin: $(\text{NH}_2, \text{C}_{10}\text{H}_{10}\text{O}_2) \text{C}_2\text{H}_2\text{O}_2 = \text{NC}_{12}\text{H}_{13}\text{O}_4$	348
Taurin: $(\text{NH}_2, \text{C}_4\text{H}_4\text{O}_2) \text{C}_2\text{H}_2\text{O}_2 = \text{NC}_4\text{H}_7\text{S}_2\text{O}_6$	349
Cystin: $\text{N}_2\text{C}_6\text{H}_6\text{S}_2\text{O}_4$	349
Tyrosin: $\text{NC}_{13}\text{H}_{11}\text{O}_6$	349
Kreatin: $\text{N}_3\text{C}_8\text{H}_9\text{O}_4$	349
Inosinic acid: $\text{HO}, \text{N}_2\text{C}_{10}\text{H}_6\text{O}_{10}$	350
Paired acids of glycocoll and taurin with cholalic acid	350
Cholic acid: $(\text{NC}_4\text{H}_3\text{O}_3) \text{C}_{48}\text{H}_{39}\text{O}_9 = \text{NC}_{52}\text{H}_{43}\text{O}_{12}$	351
Choleinic acid: $(\text{NC}_4\text{H}_5\text{S}_2\text{O}_5) \text{C}_{48}\text{H}_{35}\text{O}_9 = \text{NC}_{52}\text{H}_{43}\text{S}_2\text{O}_{14}$	352
Hyocholeic acid: $(\text{NC}_4\text{H}_4\text{O}_3), \text{C}_{50}\text{H}_{41}\text{O}_9 = \text{NC}_{54}\text{H}_{45}\text{O}_{12}$	352

V. HYDRYLS.

ORGANIC SALT BASES.

FIRST GROUP.

Nitrogen Bases.

Simple Nitrogen Bases	355
Ammonia: $\text{NH}_3$	356

BASES OF THE METHYL GROUP.

Methyl-amin: $\text{NH}_2\text{Me}, \text{NHMe}_2, \text{NHMe}_3, \text{NHMe}_4$	356
Ethyl-amin: $\text{NH}_2\text{Ae}, \text{NHAe}_2, \text{NAe}_3, \text{NAe}_4$	357
Propyl-amin: $\text{NH}_2\text{Pr}, \text{NHPr}_2, \text{NPr}_3$	357
Butyl-amin: $\text{NH}_2\text{Bu}$	357
Amyl-amin: $\text{NH}_2\text{Am}, \text{NHAm}_2, \text{NAm}_3$	357
Methyl-ethylamin: $\text{NHMeAe}, \text{NMe}_2\text{Ae}$ , etc.	357
Bases of the benzid group	358
Benzidin: $\text{NH}_2\text{Bd}$	358
Picolin: $\text{NH}_2, (\text{C}_{12}\text{H}_5)$	358
Anilin: $\text{NH}_2\text{Bd}$	358
Anilids and anilic acids	359
Formanilid: $\text{NHBd}, \text{FoO}$	359
Oxanilid: $\text{NHBd}, \text{OxO}_2$	359
Carbanilid: $\text{NHBd}, \text{CO}$	360
Sulpho-carbanilid: $\text{NHBd}, \text{CS}$	360
Sulphanilic acid: $(\text{NH}_2\text{Bd}, \text{SO}_3) \text{SO}_3$	360
Chloreycanilid	360
Oxaluranilid: $\text{NH}_2\text{Bd}, \text{N}_2\text{C}_8\text{H}_2\text{O}_6$	360
Methylanilinamin: $\text{NHMeBd}, \text{NMe}_2\text{Bd}$	360
Ethylanilinamin: $\text{NHAeBd}, \text{NAe}_2\text{Bd}$ , etc.	360
Cyananilin: $\text{NH}_2\text{Bd}, \text{Cy}$	360
Melanilin: $(\text{NH}_2\text{Bd}, \text{Cy}) \text{NH}_2\text{Bd}$	361
Bicyanomelanilin: $(\text{NHBd}, \text{Cy}_2) \text{NH}_2\text{Bd}$	361
Anilocyanic acid: $\text{HO}, \text{NC}_{14}\text{H}_4\text{O}_4$	361
Nitranilin: $\text{NH}_2\text{xBd}$	361
Chloranilin: $\text{NH}_2\text{ClBd}$	362
Bichloranilin: $\text{NH}_2, (\text{C}_{12}\text{H}_3)\text{Cl}_2$	362
Trichloranilin: $\text{NH}_2, (\text{C}_{12}\text{H}_2\text{Cl})\text{Cl}_2$	362
Naphthalidin: $\text{NH}_2, (\text{C}_8\text{H}_2) \text{Bd}$	362
Toluidin: $\text{NH}_2\text{Td}$	362
Xylidin: $\text{NH}_2\text{Xd}$	363
Cumidin: $\text{NH}_2\text{Cd}$	363
Nitromesidin: $\text{NH}_2, (\text{C}_{15}\text{H}_{10}\text{X})$	363
Cymidin: $\text{NH}_2\text{Cy}$	363

	PAGE
Chinolin: $\text{NH}_2(\text{C}_{15}\text{H}_6)$	363
Coniin: $\text{NH}(2\text{C}_8\text{H}_7)$	364
Nicotin: $\text{NH}_2(\text{N}_{20}\text{H}_{12})$	364

## PAIRED NITROGEN BASES.

<i>Bases artificially produced</i>	365
Cyanæthin: $(\text{N}_3\text{C}_{15}\text{H}_{12})\text{NH}_3$	365
Lophin: $(\text{NC}_{46}\text{H}_{13})\text{NH}_3$	365
Amarin: $(\text{NC}_{12}\text{H}_{15})\text{NH}_3$	365
Furfurin: $(\text{NC}_{30}\text{H}_9\text{O}_6)\text{NH}_3$	366
Urea: $(\text{NC}_2\text{H}_4\text{O}_2)\text{NH}_3$	366
Methyl-urea: $(\text{NC}_2\text{H}_4\text{O}_2)\text{NH}_2\text{C}_2\text{H}_5$	367
Ethyl-urea: $(\text{NC}_2\text{H}_4\text{O}_2)\text{NH}_2\text{C}_4\text{H}_9$	367
Amyl-urea: $(\text{NC}_2\text{H}_4\text{O}_2)\text{NH}_2\text{C}_{10}\text{H}_{21}$	367
Anilin-urea: $(\text{NC}_6\text{H}_5\text{O}_2)\text{NH}_2\text{C}_{12}\text{H}_5$	367
Guanin: $\text{N}_5\text{C}_{10}\text{H}_5\text{O}_2$	367
Melam: $\text{N}_{11}\text{C}_{12}\text{H}_9$	368
Melamin: $(\text{NH}_2)_3\text{N}_4\text{C}_6$	368
Ammelin: $(2\text{HO}, \text{N}_4\text{C}_6)\text{NH}_3$	368
Ammelid: $(4\text{HO}, 2\text{N}_4\text{C}_6)\text{NH}_3$	369
Caffein: $(2\text{C}_2\text{H}_5, \text{N}_2\text{C}_8\text{O}_4)\text{NH}_2\text{Me}, \text{HCy}$	369
Theobromin: $(\text{C}_2\text{H}_5, \text{N}_2\text{C}_8\text{O}_4)\text{NH}_2\text{Me}, \text{HCy}$	369
Creatinin: $(\text{N}_2\text{C}_8\text{H}_4\text{O}_2)\text{NH}_3$	370
Thiosinnamin: $(\text{NC}_8\text{H}_5\text{S}_2)\text{NH}_3$	370
Sinnamin: $(\text{NC}_8\text{H}_9)\text{NH}_3$	370
Sinapolin: $(\text{NC}_{14}\text{H}_9\text{O}_2)\text{NH}_3$	371
Thialdin: $(\text{C}_{12}\text{H}_{10}\text{S}_4)\text{NH}_3$	371
Selenäldin: $(\text{C}_{12}\text{H}_{10}\text{Se}_1)\text{NH}_3$	371
Carbothialdin: $(\text{C}_5\text{H}_2\text{S}_2)\text{NH}_3$	371
<i>Organic vegetable bases</i>	372
Aconitin: $\text{NC}_{60}\text{H}_{47}\text{O}_{14}$	373
Atropin: $\text{NC}_{31}\text{H}_{23}\text{O}_6$	373
Daturin, hyoscyamin	373
Codein: $\text{NC}_{36}\text{H}_{20}\text{O}_6$	374
Morphin: $\text{NC}_{36}\text{H}_{20}\text{O}_6$	374
Thebain: $\text{NC}_{25}\text{H}_{14}\text{O}_3$	375
Narcotin: $\text{NC}_{46}$	375
Narcein: $\text{NC}_{72}\text{H}_{20}\text{O}_{12}$	375
Pseudomorphin: $\text{NC}_{54}\text{H}_{18}\text{O}_{14}$	375
Cotarnin: $\text{NC}_{26}\text{H}_{12}\text{O}_5 + \text{aq}$	376
Narcogenin: $\text{N}_2\text{C}_{72}\text{H}_{38}\text{O}_{20}$	376
Humopinic acid: $\text{C}_{48}\text{H}_{28}\text{O}_{17}$	376
Papaverin: $\text{NC}_{40}\text{H}_{21}\text{O}_8$	376
Chelidonin: $\text{N}_2\text{C}_{40}\text{H}_{20}\text{O}_6$	377
Chelerythrin: $\text{NC}_{37}\text{H}_{16}\text{O}_5$	377
Glucin and glaucopierin	377
Solanin: $\text{NC}_{84}\text{H}_{73}\text{O}_{28}$	377
Delphinin: $\text{NC}_{27}\text{H}_{19}\text{O}_7$	378
Veratrin: $\text{NC}_{34}\text{H}_{22}\text{O}_6$	378
Subadillin: $\text{NC}_{20}\text{H}_{13}\text{O}_5$	378
Jervin: $\text{N}_2\text{C}_{60}\text{H}_{45}\text{O}_5$	378
Colchicin, emetin	378
Strychnin: $\text{N}_2\text{C}_{42}\text{H}_{22}\text{O}_4$	378
Brucin: $\text{N}_2\text{C}_{46}\text{H}_{26}\text{O}_8$	380
Kakothelin: $\text{N}_4\text{C}_{42}\text{H}_{22}\text{O}_{10}$	380
Corydalin: $\text{N}_3\text{C}_{68}\text{H}_{41}\text{O}_{22}$	381
Cinchonin: $\text{N}_2\text{C}_{40}\text{H}_{24}\text{O}_2$	381
Quinin: $\text{N}_2\text{C}_{40}\text{H}_{21}\text{O}_4$	382
Chinotin, chinidin	382
Chinoidin	383
Arcein: $\text{N}_2\text{C}_{40}\text{H}_{24}\text{O}_6$	383
Pelosin: $\text{NC}_{26}\text{H}_{21}\text{O}_5$	383

	PAGE
Berberin: $\text{NC}_{42}\text{H}_{18}\text{O}_6$ . . . . .	383
Harmalin: $\text{N}_2\text{C}_{27}\text{H}_{14}\text{O}_2$ . . . . .	383
Harmin: $\text{N}_2\text{C}_{27}\text{H}_{12}\text{O}_2$ . . . . .	383
Nitroharmalin, hydrocyanide of harmalin . . . . .	384
Behcerin: $\text{NC}_{35}\text{H}_{29}\text{O}_6$ . . . . .	384
Piperin: $\text{N}_2\text{C}_{76}\text{H}_{37}\text{O}_{10} + 2\text{aq}$ . . . . .	384
Pitoyin, Pereirin . . . . .	384
Menispermin, capsicin, etc. . . . .	385

## SECOND GROUP.

*Phosphorus Bases.*

Biphosmethyl: $\text{P}_2\text{Me}$ , Phosbimethyl: $\text{PMe}_2$ , Phosmethylamin: $\text{PH}_2\text{Me}$ , Phos-trimethyl: $\text{PMe}_3$ . . . . .	385
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## THIRD GROUP.

*Arsenic Bases.*

<i>Kakodyl</i> : $\text{Kd}=\text{AsMe}_2$ . . . . .	386
Oxide of kakodyl: $=\text{KdO}$ . . . . .	386
Kakodylic acid: $\text{HO}, \text{KdO}_3$ . . . . .	386
Protosulphide of kakodyl: $\text{KdS}$ . . . . .	387
Sulphokakodylic acid: $\text{KdS}_3$ . . . . .	387
Protochloride of kakodyl: $\text{KdCl}$ . . . . .	387
Terchloride of kakodyl: $\text{KdCl}_3$ . . . . .	388
Protobromide of kakodyl: $\text{KdBr}$ . . . . .	389
Terbromide of kakodyl: $\text{KdBr}_3$ . . . . .	389
Iodide of kakodyl: $\text{KdI}$ . . . . .	389
Fluoride of kakodyl: $\text{KdFl}$ . . . . .	389
Arsenethyl: $\text{AsAe}$ . . . . .	389
Aminoxide of arsenethyl: $(\text{AsHAe})\text{O}$ . . . . .	389
Erytrarsin: $(\text{AsHAe})\text{AsO}_3(?)$ . . . . .	390

## FOURTH GROUP.

*Antimony Bases.*

<i>Stibmethyl</i> : $\text{StMe}_3$ . . . . .	391
Stibmethylum: $\text{StMe}_4$ . . . . .	391
Oxide of stibmethylum: $(\text{StMe}_4)\text{O}$ . . . . .	391
Iodide of stibmethylum: $(\text{StMe}_4)\text{I}$ . . . . .	391
Chloride of stibmethylum: $(\text{StMe}_4)\text{Cl}$ . . . . .	391
Stibethyl: $\text{StAe}_3$ . . . . .	391
Oxide of stibethyl: $(\text{StAe}_3)\text{O}_2$ . . . . .	392
Sulphide of stibethyl: $(\text{StAe}_3)\text{S}_2$ . . . . .	392
Iodide of stibethyl: $(\text{StAe}_3)\text{I}_2$ . . . . .	392
Bromide of stibethyl: $(\text{StAe}_3)\text{Br}_2$ . . . . .	393
Chloride of stibethyl: $(\text{StAe}_3)\text{Cl}_2$ . . . . .	393
Stibethylum: $\text{StAe}_4$ . . . . .	393
Oxide of stibethylum: $(\text{StAe}_4)\text{O}$ . . . . .	393
Iodide of stibethylum: $(\text{StAe}_4)\text{I}$ . . . . .	393
Stibamyl: $\text{StAm}_3$ . . . . .	393

*Bismuth Bases.*

Bismethyl: $\text{BiAe}_3$ . . . . .	393
Platinum Bases. . . . .	394

## VI. ORGANIC COMBINATIONS OF A HIGHER ORDER.

## SPECIAL COMBINATIONS OF THE VEGETABLE KINGDOM.

1. *Tannins, or Tannic Acids.*

Catechu tannin: $3\text{HO}, \text{C}_{15}\text{H}_5\text{O}_5$ . . . . .	397
Coffee tannin: $3\text{HO}, \text{C}_{18}\text{H}_5\text{O}_6$ . . . . .	397
Morin tannin: $3\text{HO}, \text{C}_{18}\text{H}_5\text{O}_6$ . . . . .	397
Tannic acid (Gall-nut tannin): $3\text{HO}, \text{C}_{18}\text{H}_5\text{O}_9$ . . . . .	398
Kino (China) tannin . . . . .	399
Bohea tannin: $3\text{HO}, \text{C}_{18}\text{H}_7\text{O}_{10}$ . . . . .	400.

	PAGE
Products of decomposition of tannins . . . . .	400
Catechuic acid: $\text{HO}, \text{C}_{14}\text{H}_6\text{O}_6$ . . . . .	400
Viridinic acid: $\text{HO}, \text{C}_{14}\text{H}_6\text{O}_7$ . . . . .	401
Morinic acid: $2\text{HO}, \text{C}_{14}\text{H}_4\text{O}_6$ . . . . .	401
Rufimorinic acid: $\text{C}_{14}\text{H}_7\text{O}_7$ . . . . .	401
Quercitronic acid: $\text{HO}, \text{C}_{14}\text{H}_7\text{O}_8$ . . . . .	402
Gallie acid: $2\text{HO}, \text{C}_{14}\text{H}_4\text{O}_8$ . . . . .	402
Tanno-melanic acid: $2\text{HO}, \text{C}_{14}\text{H}_4\text{O}_7$ . . . . .	403
Rufin-gallie acid: $\text{C}_{14}\text{H}_4\text{O}_8$ . . . . .	403
Ellagic acid: $2\text{HO}, \text{C}_{14}\text{H}_2\text{O}_7$ . . . . .	403
Pyrotannic acids . . . . .	403
Pyromorin-tannic acid: $2\text{HO}, \text{C}_{12}\text{H}_4\text{O}_2$ . . . . .	403
Rubinic acid: $\text{C}_{12}\text{H}_4\text{O}_2$ . . . . .	404
Japonic acid: $\text{HO}, \text{C}_{12}\text{H}_4\text{O}_4$ . . . . .	404
Pyrogallie acid: $\text{C}_{12}\text{H}_6\text{O}_6$ . . . . .	404
Melan-gallie acid: $\text{HO}, \text{C}_{12}\text{H}_3\text{O}_3$ . . . . .	404
2. <i>Lichen Acids.</i>	
a. <i>Lichen acids which give orsellinic acid</i> . . . . .	406
Alphaorsellie acid: $\text{HO}, \text{C}_{16}\text{H}_8\text{O}_7$ . . . . .	406
Betaorsellie acid: $\text{HO}, \text{C}_{34}\text{H}_{16}\text{O}_{16}$ . . . . .	406
Evernic acid: $\text{HO}, \text{C}_{34}\text{H}_{16}\text{O}_{14}$ . . . . .	406
Gyrophanic acid: $\text{HO}, \text{C}_{36}\text{H}_{18}\text{O}_{15}$ . . . . .	406
Erythric acid: $2\text{HO}, \text{C}_{40}\text{H}_{22}\text{O}_{20}$ . . . . .	406
Lecanoparic acid . . . . .	407
Products of decomposition of the lichen acids . . . . .	407
Orsellinic acid: $\text{HO}, \text{C}_{16}\text{H}_8\text{O}_8$ . . . . .	407
Roccellin: $\text{C}_{18}\text{H}_8\text{O}_7$ . . . . .	407
Roccellin: $\text{HO}, \text{C}_{24}\text{H}_{22}\text{O}_5$ . . . . .	407
Pikroerythrin: $\text{C}_{24}\text{H}_{16}\text{O}_{14}$ . . . . .	407
Erythroglucin: $\text{C}_{22}\text{H}_{28}\text{O}_{22}$ . . . . .	407
Evernic acid: $\text{C}_{18}\text{H}_{10}\text{O}_8$ . . . . .	408
Orcin: $\text{C}_{14}\text{H}_8\text{O}_4 + 2\text{aq}$ . . . . .	408
Orcein: $\text{NC}_{14}\text{H}_7\text{O}_6$ . . . . .	408
Orchill and litmus . . . . .	408
b. <i>Lichen acids which contain no orsellinic acid</i> . . . . .	409
Usnic acid: $\text{C}_{34}\text{H}_{18}\text{O}_{14}$ . . . . .	409
Betaorcin: $\text{C}_{34}\text{H}_{18}\text{O}_{16}(?)$ . . . . .	410
Chrysophanic acid: $\text{HO}, \text{C}_{40}\text{H}_{16}\text{O}_{16}$ . . . . .	410
Cetraric acid: $\text{C}_{34}\text{H}_{16}\text{O}_{15}$ . . . . .	410
Indigo . . . . .	411
Indigo-blue: $\text{Ig}=\text{NC}_{16}\text{H}_5\text{O}_2$ . . . . .	412
Purpur-sulphuric acid: $\text{HO}, (\text{Ig}_2, \text{SO}_3) \sim \text{SO}_3$ . . . . .	413
Indigo-blue-sulphuric acid: $\text{HO}, (\text{Ig}, \text{SO}_2) \sim \text{SO}_3$ . . . . .	413
Indigo-white: $\text{IgH}=\text{NC}_{16}\text{H}_6\text{O}_2$ . . . . .	414
Isatin: $\text{IgO}_2=\text{NC}_{16}\text{H}_5\text{O}_4$ . . . . .	414
Isatyd: $\text{NC}_{16}\text{H}_6\text{O}_4$ . . . . .	414
Sulphisatin: $\text{NC}_{16}\text{H}_5\text{O}_2\text{S}_2$ . . . . .	414
Isaten: $\text{NC}_{16}\text{H}_6\text{O}_3$ . . . . .	415
Sulphisaten: $\text{NC}_{16}\text{H}_6\text{O}_3\text{S}$ . . . . .	415
Chlorisatin: $\text{NC}_{16}\text{H}_4\text{ClO}_4$ . . . . .	415
Bichlorisatin: $\text{NC}_{16}\text{H}_3\text{Cl}_2\text{O}_4$ , etc. . . . .	415
3. <i>Coloring Matters.</i>	
Chlorophyl: $\text{NC}_{18}\text{H}_9\text{O}_8$ . . . . .	417
Xanthophyl, Erythrophyl . . . . .	418
Rubian . . . . .	418
Alizarin: $\text{C}_{20}\text{H}_6\text{O}_6 + 4\text{aq}$ . . . . .	419
Purpurin: $\text{C}_{18}\text{H}_6\text{O}_6$ . . . . .	419
Garancin . . . . .	420
Anchusin: $\text{C}_{35}\text{H}_{20}\text{O}_8$ . . . . .	420
Brazilin: $\text{C}_{36}\text{H}_{14}\text{O}_{12}$ . . . . .	420
Carthamin: $\text{C}_{14}\text{H}_8\text{O}_7$ . . . . .	420

	PAGE
Carminic acid: $C_{28}H_{14}O_{16}$	421
Hæmatoxylin: $C_{40}H_{17}O_{15}$	421
Hæmatein: $C_{40}H_{14}O_{15}$	422
Santalin: $HO, C_{30}H_{13}O_9$	422
Curcumin	422
Euxanthin: $C_{40}H_{16}O_{21}$	422
Euxanthone: $C_{18}H_4O_4$	423
Nitropurpuric acid: $C_{40}H_{15}O_{21}X$	423
Luteolin	423
Orellin: $C_{16}H_{13}O_2$	423
Gentianin: $C_{14}H_5O_5$	423
Plumbagin	424
Chrysorhamnin: $C_{23}H_{11}O_{11}$	424
Xanthorhamnin: $C_{23}H_{12}O_{14}$	424
Juice-green	424

## 4. Indifferent Colorless Vegetable Matters.

*Bitter Principles.*

Phloridzin: $C_{21}H_{16}O_{14}$	425
Phloretin: $C_{12}H_8O_4$	426
Phloridzein: $NC_{21}H_{19}O_8$	426
Salicin: $C_{26}H_{18}O_{14}$	426
Helicin: $C_{52}H_{35}O_{31}$	427
Helicoidin: $C_{52}H_{34}O_{28}$	427
Saliretin: $C_{14}H_6O_2$	427
Rutilin: $C_{23}H_{12}O_4$	427
Rufin: $C_{28}H_{14}O_{10}$	427
Olivin: $C_{23}H_{12}O_8$	427
Caincin: $C_{23}H_{13}O_{21}$	427
Olivil: $C_{28}H_{18}O_{10}$	428
Amygdalin: $NC_{40}H_{27}O_{22}$	428
Myronic acid	428
Athamantin: $C_{24}H_{15}O_7$	429
Peucedanin: $C_{12}H_{12}O_6$	429
Oresolon: $C_{14}H_5O_3$	429
Absynthiin: $C_{16}H_{10}O_4$	429
Aloin: $HO, C_{34}H_{18}O_{14}$	430
Appiin: $C_{24}H_{14}O_{13}$	430
Aesculin: $C_{16}H_9O_{10}$	430
Anthiarin: $C_{14}H_{10}O_5$	430
Cocculin: $C_{10}H_6O_4$	431
Columbin: $C_{42}H_{22}O_{14}$	431
Chinovin: $HO, C_{38}H_{29}O_9$	431
Limonin: $C_{42}H_{25}O_{13}$	431
Meconin: $C_{20}H_{10}O_8$	431
Quassiin: $C_{20}H_{12}O_5$	431
Santonin: $C_{30}H_{18}O_6$	432
Saponin: $C_{26}H_{24}O_{16}$	432
Senegin: $C_{22}H_{18}O_{11}$	432

*Sweet Principles.*

Mannit: $C_{12}H_{14}O_{12}$	432
Nitromannit: $C_{12}H_8X_6O_{12}$	433
Glycyrrhizin: $C_{16}H_{12}O_6$	433
Dulcose: $C_{12}H_{14}O_{12}$	433
Glycerin: $C_6H_8O_6$	433

## COMMON VEGETABLE AND ANIMAL MATTERS.

## 1. Non-nitrogenous Combinations.

*Carbohydrates.*

Cellulose: $C_{12}H_{10}O_{10}$	438
Nitrocellulose: $C_{12}H_7X_3O_{10}$	438
Cork-substance	439

	PAGE
Starch species . . . . .	439
Amylum } $C_{12}H_{10}O_{10}$ . . . . .	439, 440, 441
Inulin } . . . . .	
Lichenin } . . . . .	
Gum species . . . . .	441
Dextrine } $C_{12}H_{10}O_{10}$ . . . . .	441, 442
Arabin } . . . . .	
Vegetable gluten } . . . . .	
Sugar species . . . . .	442
Milk-sugar } $C_{12}H_{10}O_{10}$ . . . . .	442, 443
Cane-sugar } . . . . .	
Fruit-sugar } $C_{12}H_{12}O_{12}$ . . . . .	443, 444
Grape-sugar } . . . . .	
Inosit . . . . .	444
<i>Pectin-substances.</i>	
Pectase . . . . .	445
Pectose . . . . .	445
Pectin: $C_{61}H_{40}O_{56}+8Aq$ . . . . .	445
Parapectin } $C_{64}H_{40}O_{56}+8Aq$ . . . . .	446
Metapectin } . . . . .	
Pectosic acid: $C_{32}H_{20}O_{28}+3Aq$ . . . . .	446
Pectic acid: $C_{32}H_{20}O_{28}+2Aq$ . . . . .	446
Parapectic acid: $C_{24}H_{15}O_{21}+2Aq$ . . . . .	446
Metapectic acid: $C_8H_5O_7+2Aq$ . . . . .	446
<b>2. Nitrogenous Combinations.</b>	
<i>Protein-substances.</i>	
<i>Protein combinations of the vegetable kingdom</i> . . . . .	451
Legumin . . . . .	451
Vegetable gluten . . . . .	451
Synaptase . . . . .	451
Myrosin . . . . .	451
Vegetable albumen . . . . .	452
<i>Protein combinations of the animal kingdom</i> . . . . .	452
Albumen . . . . .	452
Fibrin . . . . .	452
Bioxyprotein . . . . .	453
Trioxyprotein . . . . .	453
Vitellin . . . . .	454
Casein . . . . .	454
Crystallin . . . . .	454
Globulin . . . . .	455
Horn-tissues . . . . .	455
Fibroin, chitin . . . . .	455
<i>Tissues affording glue and chondrin</i> . . . . .	455
Glue: $N_2C_{13}H_{10}O_5$ . . . . .	456
Chondrin: $N_4C_{32}H_{26}O_{14}$ . . . . .	457
<i>Animal coloring matters</i> . . . . .	457
Hæmatin: $N_3C_{44}H_{22}O_6Fe$ . . . . .	457
Hæmaphæin . . . . .	457
Hæmatoïdin . . . . .	458
Pigmentum nigrum oculi . . . . .	458
Gall-brown . . . . .	458
Gall-yellow . . . . .	458

## VII. GENERAL PRODUCTS OF DECOMPOSITION.

### *Ulmín-substances and humín-substances.*

Ulmín-substances: $C_{40}H_{16}O_{14}$ . . . . .	460
Humín-substances: $C_{40}H_{15}O_{12}$ . . . . .	460
Crenic acid: $C_{14}H_{15}O_{19}$ . . . . .	461
Apocrenic acid: $C_{48}H_{12}O_{24}$ . . . . .	461
Extract-sediment . . . . .	461
Brown coal and bituminous coal . . . . .	461



# CONSTITUTION OF THE ORGANIC COMPOUNDS,

AND

## COMPARISON WITH THE INORGANIC.

THE organic compounds which constitute the great mass of plants and animals differ from the inorganic:—

1. In the small number of the elements in which the former consist.

2. In the complicated atomic proportions in which these few elements in the organic are found to unite; and,

3. In the impossibility of producing organic matter direct from its elements, since the co-operation of vitality, or of the other predisposing forces, is necessary to its formation.

The essential elements which form the great mass of plants and animals are carbon, hydrogen, nitrogen, and oxygen.

Carbon is found in all organic combinations; part united with oxygen or hydrogen, part with hydrogen and oxygen, or yet at the same time with nitrogen.

Elements of the organic compounds.

Several combinations contain, also, phosphorus and sulphur. Substances are artificially produced having other metallic as well as non-metallic elements, as the halogens,\* sulphur, selenium, tellurium, phosphorus, arsenic, antimony, and bismuth, which, in relation to atomic proportions and other characteristics, entirely agree with the natural, and are, therefore, classed with organic compounds. Besides, in natural organic matter inorganic salts often occur; indeed, several of them are indispensable to the growth and development of plants and animals. Yet most of these inorganic combinations suffer themselves to be withdrawn from the organic without destroying the organism, and thence do not necessarily belong to the peculiar organic constitution. Whilst in most inorganic compounds of the first order only 1 atom of an element is united with 1, 2, 3, 4, or 5 atoms of another, in the organic a much greater number occur, particularly of the carbon and hydrogen atoms. Thus, sulphuric acid consists of  $\text{SO}_3$ , boracic acid of  $\text{Bo O}_3$ ; acetic acid, on the contrary, =  $\text{C}_4\text{H}_3\text{O}_3$ . In nitric acid, five atoms of oxygen com-

Atomic proportions of the organic compounds.

\* Halogens = Chlorine, Bromine, Iodine, and Fluorine.

bine with one of nitrogen, and in salicylic acid the same number of atoms of oxygen unite with 14 atoms carbon and 5 atoms hydrogen. Thus, valerianic acid consists of  $C_{10}H_9O_3$ , margaric acid of  $C_{34}H_{33}O_3$ . Alcohol corresponds to the formula  $C_4H_6O_2$ , and spirit of amyl  $C_{10}H_{12}O_2$ . Hence the difference between the organic and inorganic compounds is not in the diversity of the elements, but in the different manner of their union. The multiplicity of the inorganic compounds is dependent upon the number of the elements, and that of the organic upon the property, particularly of carbon and hydrogen, of uniting in greatly complicated proportions. Oxygen alone enters into organic bodies in the same atomic proportions as in the inorganic; in none of the former does it suffice for the full oxidation of the carbon and hydrogen atoms. If the chemical formula gives only the relative atomic proportions of the elements of a compound, it is called *empirical*; if it express the constitution of the compound it is called *rational*. Thus the empirical formula for sulphate of potassa is  $KSO_4$ ; the rational, on the contrary, is  $KO,SO_3$ . If we compare with sulphate of potassa acetate of potassa  $KO, C_4H_3O_3$ , a quantity of acetic acid is given for  $KO$ , which, like sulphuric acid, contains 3 atoms of oxygen, but with these  $C_4H_3$  a complex atom of seven simple atoms is combined, which in acetic acid corresponds to  $S$  in  $SO_3$ ; in the same manner in valerianic acid with  $O_3$  are united  $C_{10}H_9=19$  simple atoms. If we compare with the sulphate of potassa the sulphate of the ethyl  $C_4H_5O,SO_3$ , it is evident that potassa and oxide of ethyl each contain one atom of oxygen; but whilst this atom in potassa is combined with one atom potassium, in the oxide of ethyl it unites with  $C_4H_5$ ; therefore in all with 9 simple atoms which correspond to the 1 atom of potassium. Like potassium, this complexity of 9 atoms gives with sulphur the halogens, &c., the compounds corresponding to the oxides. These complex atoms, therefore, behave in the organic substances like the elements in the inorganic. Thus,  $C_4H_3=S$  and  $C_4H_5=K$ . The rational formula for acetic acid is hence  $(C_4H_3)O_3$ , for oxide of ethyl  $(C_4H_5)O$ , and for acetate of ethyl  $(C_4H_5)O, (C_4H_3)O_3$ .

Empiric and  
rational formulae.

If an atom of an element unite with one, two, three, or more atoms of another, or if it give with different elements a series of equivalent compounds, it is thence called the radical of the different compounds. Thus, nitrogen is the radical in  $NO, NO_2, NO_3, NO_4, NO_5$ . In the same way, potassium appears as radical in  $KO, KS, KCl, KBr$ . The idea of a radical is indeed only relative, and one and the same element, according as it takes place in the chemical series, and as the elements with which it is united can enter as a radical but also appear as an element in the combination in which the atom with which it is united plays the part of a radical; thus in chloric acid  $ClO_3$ , chlorine is the radical, and in chloride of sodium  $NaCl$

Idea of a radical. Simple radicals.

sodium is the radical. Potassium alone in its compounds takes the part of a radical, whilst oxygen never appears as such. Thus all metallic elements do not behave to oxygen as radicals, whilst the halogens, in their combinations with sulphur, selenium, tellurium, nitrogen, phosphorus, arsenic, antimony, carbon, boron, and silicon, act the part of oxygen. Sulphur, selenium, and tellurium, play the same part in their combinations with the succeeding elements. In a word, in an inorganic compound consisting of two elements the positive is generally the radical; but since a positive element is negative towards a positive, and a negative appears positive towards a negative, it follows that the same element, in its combinations, according to the substances with which it is united, can take a twofold place. Since the radicals in the inorganic compounds are simple elementary atoms, they are called *simple radicals*.

If an element as a radical with other elements which in chemical relation belong to a group, give a series of combinations of the same atomic number, these combinations are called corresponding or equivalent. Thus,  $\text{PO}_3, \text{PCl}_3, \text{PBr}_3, \text{PI}_3$ , and, farther,  $\text{KO}, \text{KS}, \text{KCl}, \text{KBr}$ , are corresponding combinations, and appear as equivalent constituents in the compounds with P, the elements  $\text{O}_3, \text{Cl}_3, \text{Br}_3, \text{I}_3$ . The same is true for  $\text{O}, \text{S}, \text{Cl}, \text{Br}$ , in the corresponding compounds of potassium. Thus,  $\text{FeO}, \text{MnO}, \text{CoO}, \text{NiO}$ , are corresponding compounds, only the radicals in these are the corresponding elements. These corresponding elements can alternately enter into the combinations without the character of the latter suffering thereby an essential change. Thus, oxy-chlorophosphoric acid  $\text{P} \begin{Bmatrix} \text{O}_3 \\ \text{Cl}_2 \end{Bmatrix}$  exhibits phosphoric acid in which  $\text{O}_2$  is replaced by  $\text{Cl}_2$ ; if we treat the same with water we obtain  $\text{PO}_3$ , and  $2\text{HCl}$ . Thus, amide of potassium  $\text{NH}_2\text{K}$  appears as ammonia, in which one atom of hydrogen is substituted by one atom of potassium; if we add water to the above compound, we obtain by decomposition of one atom of water  $\text{KO}$  and  $\text{NH}_3$ .

According to the elements which are united with the radicals in the inorganic compounds, these compounds separate into *oxygen-compounds*, *sulphur-compounds*, *haloid-compounds*, *oxychlor-compounds*, *oxybrom-compounds*, *oxychlorbrom-compounds*, and according to the degrees of union into combinations of the *first*, *second*, or *higher orders*.

If from the empirical formula of acetic acid  $\text{C}_4\text{H}_5\text{O}_3$  we subtract the oxygen, there remains  $\text{C}_4\text{H}_3$ ; this compound body, as has already been shown, has the same signification in acetic acid as phosphorus in  $\text{PO}_3$ , or boron in  $\text{BoO}_3$ . As boron forms compounds with chlorine, bromine, and sul-

Entrance of homogeneous elements in the compounds.

Substitution.

Division of the organic compounds.

Compound radicals.

phur, which are equivalent to boracic acid, so also the complex atom  $C_4H_3$  unites with the above-mentioned elements in the same atomic proportions as with oxygen. With the same right that boron, in its combination with  $O_3, Cl_3, Br_3, S_3$ , appears as a radical, must also  $C_4H_3$  be considered as such in  $(C_4H_3)O_3$ ;  $(C_4H_3)Cl_3$ ;  $(C_4H_3)Br_3$ . If we treat  $BoCl_3$  with potassa we obtain  $3KCl$  and  $KO, BoO_3$ , and if we let potassa act upon  $(C_4H_3)Cl_3$  we obtain  $3KCl$  and  $KO, (C_4H_3)O_3$ . Since the body  $C_4H_3$  only in its compounds behaves entirely like an element playing the part of a radical, therefore it is called a *compound* or *organic radical*. The organic compounds suffer themselves to be led back to their compound radicals as the inorganic to their simple radicals. These compound radicals behave, in chemical relation, quite like elements; in their combining proportions they follow precisely the same laws in accordance with which the elementary materials combine amongst themselves; they give with  $O, S, Cl, Br, I$ , etc., equivalent series, often uniting with these substances in various proportions, and can represent, entirely or in part, chemically homogeneous elements in the compounds. Thus, for example, the compound  $NH_2(C_4H_5)$  corresponds to amide of potassium. They exhibit, for instance, ammonia in which the third atom of hydrogen is substituted by  $C_4H_5$ . The chemical characters of these compounds accord with those of the inorganic, and like the latter they separate into *oxygen-compounds*, *sulphur-compounds*, *haloid-compounds*, *oxychlor-compounds*, etc., as well as into combinations of the *first*, *second*, and higher *orders*. In all compounds the organic radicals are to be viewed as a whole, and the consideration of the individual atoms thereof is of secondary moment.

Primary radicals.

Since the elements which occur in organic compounds in plants and animals are *carbon*, *nitrogen*, *hydrogen*, and *oxygen*, and the latter never enters as a constituent of a radical, it follows that only the first three elements, part in singular, part in binary and ternary union, can be the constituents of radicals which are the groundwork of natural organic compounds; all radicals which are composed of the above-named elements, are therefore called *primary*. But it has been already intimated, that artificial radicals are obtained in which also other elements, and particularly the halogens—nay, even compound bodies, as  $NO_4$ , enter as constituents. If we treat  $PH_3$  with chlorine, we obtain  $PCl_3$  and  $3HCl$ ; in the same manner the

Derived radicals.

radical of acetic acid  $C_4H_3$ , goes over by the same treatment into  $C_4Cl_3$ . This complex atom behaves towards other elements like  $C_4H_3$ ; it combines with  $O_3, Cl_3, Br_3$ ; if we treat the compound  $(C_4Cl_3)Cl_3$  with potassa, we obtain  $3KCl$  and  $(C_4Cl_3)O_3$ ; therefore, only the chlorine atoms, which do not occur in the radical, are replaced by the same number of atoms of oxygen. Hence it follows with certainty that



chlorine is variously united in the combination. As has already been remarked, the idea of a radical is not absolute; in the compound  $(C_4H_3)Cl_3$  the radical is  $C_4H_3$ , even as in  $BoO_3$  boron, or hydrogen in  $HCl$ ; on the contrary, in  $(C_4Cl_3)O_3$  chlorine is a constituent of the radical, and plays in this connection the part of chlorine in chloric acid. Bromine, iodine, sulphur, etc., behave in the same manner as chlorine. Since these radicals always arise by the decomposition of the primaries, they may be considered as *derived radicals*. In the derived radical  $C_4Cl_3$  the hydrogen in  $C_4H_3$  is completely substituted by chlorine, hence the substitution is total. Very often, indeed, only a partial substitution of hydrogen takes place, and then we obtain the partially derived radicals, namely, such as contain chlorine in addition to carbon and hydrogen. Thus, the radical of valerianic acid consists of  $C_{10}H_9$ ; this by the action of chlorine, goes over into first  $C_{10}H_7Cl_2$ , and then into  $C_{10}H_5Cl_4$ . That the chlorine atoms in these radicals really enter as constituents is proved by the fact that, by treatment with potassa, the chlorine cannot be absorbed, as would certainly be the case if the body  $C_{10}H_7Cl_2$  were a compound of  $C_{10}H_7$  with  $Cl_2$ —in that case we must obtain  $(C_{10}H_7)O_2$ , but that does not occur.

Such partial substitutions almost always occur when the primary radical consists of a great number of carbon and hydrogen atoms. All derived radicals, equally, if the substitution be partial or total, give the same compounds as the primaries out of which they arise, only the derived have a more negative character than the primary, in proportion as the replacement of H by Cl, Br, I is the more complete. All primary radicals, and the thence arising derived radicals, like those of the corresponding compounds, form as it were a natural family.

Like the elements in the inorganic compounds, the organic radicals obtain fixed names and symbols. The names of the primary radicals are formed quite arbitrarily, according to their occurrence, formation, constitution, or any distinguished property. Thus, the radical of acetic acid  $C_4H_3$  is called *acetyl*=Ac, and that of oxide of ethyl  $C_4H_5$  *ethyl*=Ae; the rational formula of acetic acid is thence  $AcO_3$ , that of oxide of ethyl  $AeO$ , and the acetate of oxide of ethyl  $AeO, AcO_3=KO, SO_3$ .

Names and symbols of the compound radicals.

Thus is	Methyl	= $C_2H_3$	= Me	Radical of	wood-spirit.
" "	Ethyl	= $C_4H_5$	= Ae	" "	alcohol.
" "	Amyl	= $C_{10}H_{11}$	= Am	" "	amyl spirit.
" "	Acetyl	= $C_4H_3$	= Ac	" "	acetic acid.
" "	Butyryl	= $C_8H_7$	= Bu	" "	butyric acid.
" "	Valeryl	= $C_{10}H_9$	= Va	" "	valerianic acid.
" "	Benzoyl	= $C_{10}H_5$	= Bz	" "	benzoic acid.

In naming the derived radicals, the name of the primary whence they are formed is retained, and the name of the element which substitutes the hydrogen is prefixed. Thus chloracetyl ( $C_4Cl_3$ ) corresponds to acetyl ( $C_4H_3$ ), chloracetic acid ( $C_4Cl_3$ ) $O_3$  to acetic acid ( $C_4H_3$ ) $O_3$ , and chloride of chloracetyl ( $C_4Cl_3$ ) $Cl_3$  to chloride of acetyl ( $C_4H_3$ ) $Cl_3$ . The symbol for chloracetyl may be  $^{Cl}Ac$ ; hence the rational formula for chloride of acetyl is  $AcCl_3$ , that for chloride of chloracetyl  $^{Cl}AcCl_3$ , and that for bromide of chloracetyl  $^{Cl}AcBr_3$ ; generally, the rational elementary formula is given in that of the derived radicals. If the replacement of hydrogen by the halogens be only partial, then will the number of atoms which take the place of the hydrogen be given by the Greek\* numerals; thus bichlorvalerian acid denotes valerianic acid, in which 2 atoms of hydrogen are substituted by 2 atoms of chlorine; in the tetrachlorvaleric acid,  $H_4$  are substituted by  $Cl_4$ .

According to the number of elements whence the primary radicals arise, these radicals separate into

- Division of the radicals.
- Carbyls, or radicals, which consist of many individual atoms of carbon; the radicals of this group terminate in *yl*, as Oxetyl =  $C_2 = Ox$ .
  - Hydrocarbyls; they consist of carbon and hydrogen, and also terminate in *yl*, as Acetyl =  $C_4H_3 = Ac$ . Ethyl =  $C_4H_5 = Ae$ ; Benzoyl =  $C_{14}H_5 = Bz$ .
  - Azocarbyls; or radicals consisting of nitrogen and carbon; they terminate in *an*†, e. g. paraban =  $N_2C_6 = Pr$ .
  - Hydroazocarbyls; radicals consisting of nitrogen, carbon, and hydrogen; they terminate in *en*, as *uren* =  $NC_2H = Ur$ .

The greatly predominating class of organic compounds belong to the Hydrocarbyls.

The derived radicals all terminate in *yl*, and according as a complete or partial substitution of hydrogen by the halogens has taken place, they may be classed into *Chlorcarbyls*, *Bromocarbyls*, *Iodocarbyls*, *Chlorhydrocarbyls*, &c. &c.

Organic molecules. According to the above, the organic radicals are, as it were, the elements of the organic compounds; we can hence consider them as compound elements with the same reason that we speak of compound atoms. Better, indeed, might be the appellation "organic molecule," under which

\* As no author uniformly follows a rule in the use of numerical prefixes, the translator has not thought it expedient to change the terms *bi*, *tri*, etc., originally used in this work. Yet would it not be a great aid to science if chemical technicalities could be regarded as belonging to a universal language, and chemists were invariably to employ *duo*, *tri*, *tetra*, *penta*, *hexa*, etc., in reference to metals in primary compounds; and to bases and passive elements in secondary and higher combinations, applying *bi*, *ter*, *quad*, *quin*, *sex*, etc., to non-metallic substances, acids, and active elements?—D. B.

† Doubtless *an* will be employed in English as the termination of all new radicals consisting of nitrogen and carbon; cyanogen, now an exception, may hereafter be written *cyan*, as in German.



is to be understood a complex atom, often homogeneous as well as heterogeneous, which in its combinations assumes the part of a simple element, and this complex atom, in the combinations which it forms, is to be viewed as an indivisible whole. The organic molecules represent simple organic radicals, but if two or more simple molecules enter together in such a manner that only one of them determines the combining capacity of the compound molecules, the other, on the contrary, accompanying it in all its combinations, but behaving itself in the same entirely indifferent, then are formed *paired radicals*, in which an *active* and a *passive* molecule are discerned; the active determines the combining capacity, the passive takes no part therein, and is called the *Pairling*. This passive molecule, in the exhibition of the formula is inclosed in brackets, and connected to the active molecule by a hyphen e. g.  $(C_4H_2)^-C_2H$  exhibits a radical which consists of the passive  $C_4H_2$  and the active  $C_2H$ . Even organic compounds of a higher order can assume the part of pairlings; thus the simple molecule methyl  $=C_2H_3$  unites with  $SO_2$  to form  $C_2H_3,SO_2$  and this compound unites with  $SO_3$  to form a paired acid  $=(C_2H_3,SO_2)^-SO_3$ . If two simple organic molecules or radicals so unite that each retains its combining capacity, *double radicals* are thus formed; thus the radical of succinic acid is a double radical  $=C_6H_3, C_2H$ ; if it combine with oxygen we obtain  $(C_6H_3)O_3^-(C_2H)O_3 = C_8H_4O_6$ ; succinic acid saturates two atoms base; it is a real double acid.

If organic compounds, endowed with various properties, have, in absolute as well as relative connection, a corresponding elementary constitution, then are they called *isomeric*. Isomeric molecules are, therefore, such as are constituted alike, uniting in the same atomic proportions with other bodies, but yet producing different compounds. In these isomeric radicals it is granted, however, that the individual atoms which form the compound molecule have united with each other in various ways; the difference in the properties of the radicals is hence dependent upon the different grouping of the atoms; therefore, in the exact sense, no isomeric radicals exist. Thus the composition of benzoic acid  $(C_{14}H_5)O_3$  is entirely the same in elementary relation as that of salicylic acid, but the latter, in a potassa solution exposed to the air, decomposes into acetic and melanic acid; hence salicylic acid contains a paired radical  $=(C_4H_2)^-C_{10}H_3$ , whilst the radical of benzoic acid is  $C_{14}H_5$ . In many cases, only the *absolute* proportions of the elements in the organic molecules are the same, whilst the *relative* differ; such radicals are called *polymeric*, but the polymeric are also often founded upon a different union of the atoms. The polymeric result from the different atomic weights when the

Paired  
radicals.

Double  
radicals.

Isomeric, polymeric, and metameric radicals and compounds.

radicals have the capacity to form combinations with other bodies, and from the different specific gravity of their gases when they go over, in a higher temperature, into the gaseous state without decomposition. Thus, turpentine oil  $C_{10}H_8$  and colophen  $C_{20}H_{16}$  are polymeric bodies; the specific gravity of colophen gas is twice that of turpentine oil. If in different combinations of a higher order, the absolute and the relative number of individual elementary atoms are the same, but their proximate constituents different, then the combinations are *metameric*. Thus, hydrated acetic acid  $HO, (C_4H_3)O_3 = C_4H_4O_4$  is metameric with formate of methyl  $(C_2H_3)O, (C_2H)O_3 = C_4H_4O_4$ ; acetate of methyl  $(C_2H_3)O, (C_4H_3)O_3 = C_6H_6O_4$  is metameric with formate of ethyl  $(C_4H_5)O, (C_2H)O_3 = C_6H_6O_4$  and with hydrate of metacetic acid  $HO, (C_6H_5)O_3 = C_6H_6O_4$ .

According to the present state of organic chemistry, it may be received as certain, that the different properties of most of the compounds considered as isomeric, originate from various proximate constituents, and are therefore metameric. It is the task of organic chemistry, whether the organic compounds occur already formed in plants and animals, or are obtained artificially, to trace back their primary, derived, and paired radicals, and to investigate the conditions under which they form and are able to be united in higher combinations. Chemistry of organic combinations and chemistry of organic radicals have thence the same meaning. Only a few organic radicals have as yet been obtained isolated; by reason of their compound nature they mostly separate by the attempt to withdraw them from their combinations into new radicals and combinations generally less complex. By the use of more suitable means of reduction and electrical influence, chemists have lately succeeded in isolating those radicals most important, and whose bearing is most direct upon the theories of organic chemistry, thus establishing the fact of their existence beyond a doubt.

Task of organic chemistry.

Isolation of the radicals.

Relations of affinity between the elements of organic radicals and compounds.

Against the theories of the organic radicals as generally explained (whose confirmation will hereafter be given), it has been objected that organic radicals consisting of carbon and hydrogen cannot possibly combine as a whole with oxygen, because, as is known, the affinity of oxygen for carbon, as well as for hydrogen, is so considerably greater than that between the elements of the received radicals. The doctrine of the difference in the strength of the affinity of the elements is supported by many facts, and it is probable that it stands in intimate connection with the atomic weights of the elements belonging to a group; thus the atomic weights of potassium, sodium, lithium, barium, strontium, and calcium are proportionate to their strength of affinity. We

observe the same on the negative side between chlorine, bromine, and iodine, or sulphur, selenium, and tellurium, only with this difference, that in the positive series the greatest atomic weight corresponds to the most positive character; in the negative, on the contrary, the least atomic weight coincides with the strongest negative relations. Thus, elements of the same chemical affinity, as iron, chromium, manganese, cobalt, and nickel, have atomic weights included in narrow limits.

These different relations of affinity may be distinctly observed if we bring together one element with a few others of the same group, either negative or positive. But few elements combine at the ordinary temperature; in the greater number, the affinity must be first increased by heat. If we bring 1 atom of potassium into a mixture of 1 atom of chlorine and 6 atoms oxygen gas, there is formed chloride of potassium, and all the oxygen remains behind; hence, the potassium possesses a greater affinity for chlorine than for oxygen. This proportion of affinity of the elements towards each other, which, indeed, by various conditions, as by cohesion, inclination to the gasiform state, etc., suffers distinct modifications, can be viewed under *Primitive Affinity*.

Primitive affinity.

Although the affinity of potassium for oxygen is weaker than for chlorine; and, moreover, the combinations of chlorine with oxygen result only in an indirect way, yet, thus can potassa unite with chloric acid to form a salt,  $\text{KO}, \text{ClO}_3$ . In accordance with primitive affinity, chloride of potassium must immediately be formed under separation of oxygen. Thus, nitrous acid combines with ammonia, although the primitive affinity of oxygen for hydrogen is considerably greater than that of nitrogen for oxygen and for hydrogen. The cause of the combining property of the above-mentioned bodies lies in the opposite chemical character of potassa and chloric acid, as well as in that of ammonia and nitrous acid. These chemical relations act in opposition to the original affinities; this is the reason why hyperchloric acid is more stable than chloric acid. If we bring chlorine into an aqueous solution of potassa, we obtain chloride of potassium and chlorate of potassa. In the formation of the latter, the basic character of potassa is the cause of the union of chlorine with oxygen; but if we heat the chlorate of potassa, the original affinity of chlorine for potassium will be increased by the heat; it will now overpower the chemical characters, and we obtain by evolution of oxygen gas chloride of potassium; upon the same grounds the nitrate of ammonia decomposes by heat into water and nitrogen gas. All inorganic combinations in which the elements are not united with each other according to their primitive proportions of affinity, but by the opposite chemical characters of the proximate constituents, are decomposed if in any

Original affinity modified by the chemical character of the compound.

way the original affinity attain to a certain degree of tension; each combination carries thus within itself the germ of decomposition. In all combinations whose organic radicals consist of carbon, and hydrogen with oxygen, chlorine, and bromine, the elements are not combined according to their original affinities. Formic acid consists of  $C_2H + O_3$ . In accordance with the above-named affinity the same must consist of  $C_2O_2 + HO$ . But the radical  $C_2H$  behaves to oxygen as ammonia to nitrous acid; it is decidedly in comparison to oxygen chemically positive; and this opposite chemical character limits the combination. But if we treat formic acid with sulphuric acid, which is known to have a great affinity for water, and therefore acts in the same manner as heat, it thus separates into water and oxide of carbon. All organic combinations with O, Cl, Br, etc., are decomposed so soon as their original affinity, whether it be by warmth or other influences, is so increased that it triumphs over the chemical characters of the proximate constituents.

#### FORMATION OF ORGANIC COMBINATIONS.

Most of the inorganic combinations can be produced directly from their elements; and analytical action can again reduce them into their proximate and their remote constituents. In the same manner the organic cannot be obtained. The formation of the latter results

##### *a. By decomposition of inorganic Compounds.*

1. By the vitality of plants under the co-operation of light.
2. Without the co-operation of vitality.

##### *b. By decomposition arising out of organic Compounds by means of manifold influences.*

The inorganic materials for the formation of organic compounds under the influence of the vitality of plants, are carbonic acid, water, and ammonia. As is known, the lower plants, as the fungi, consist of single cells, each of which represents the plant itself; by the union of these cells the cellular tissue of the higher plants is formed. These cells are the most important organs of plants; in them, under the action of the sunlight, and particularly of the yellow and green rays, the formation of the organic compounds takes place. The green parts of plants, particularly the leaves, possess the power of decomposing water and the carbonic acid of the air; consequently overcoming the original affinities by which the elements in these combinations are united, and of uniting the carbon of carbonic acid with the hydrogen of water to form organic radicals or molecules, which either combine with each other, or unite with one part of the oxygen withdrawn from

Formation of organic compounds under the influence of the vitality of plants.



carbonic acid and water, whilst the other part escapes into the atmosphere. In most cases, the volumes of oxygen gas set free are equal to the volumes of carbonic acid absorbed by the plants; and if this, in the formation of certain organic compounds, is not the case, yet the result in the entire vegetable kingdom will agree with the above. Plants prevent the accumulation of carbonic acid in the air, and mainly cause the atmosphere to remain the same. It is true, the leaves absorb oxygen during the night, and evolve carbonic acid; yet the parts of plants not green receive oxygen by day and night, and thence give forth carbonic acid. But the quantity of oxygen gas which the plants use in the formation of carbonic acid, is much less than that which the green parts of the same emit by day. If the constituents of ammonia, which by continual decomposition of animal matter arises in great quantities, take part at once in the formation of organic compounds, so arise nitrogenous organic radicals. A part of the material which is necessary to the existence and growth of plants, they also obtain from the residue of organic matter already attacked by decomposition, without previous formation of carbonic acid and ammonia.\* The compounds which are formed in plants suffer during the growth of the latter continual changes, as well in physical as in chemical relation. The ascertaining of the conditions under which the formation of organic matters in plants occurs, as well as the changes in the same which they continually undergo, is the object of the physiology of plants, and this is the basis of rational agriculture.

Without the influence of the vitality of plants, as yet, only a few organic compounds can be produced; and it was believed, until recently, that organic bodies could only be formed through the inherent vital powers of plants. This view is completely refuted by the new researches in the province of organic chemistry, since chemists have succeeded in producing, artificially, complete organic combination out of inorganic matter, and precisely such as occur in

Formation of organic compounds from inorganic matter without co-operation of the vitality of plants.  
Artificial formation.

\* Each plant, after complete burning, leaves behind a certain quantity of matter as ashes. The material of these compounds originates in the soil from which the same grow. In what way the inorganic matters are united to the organic is not yet ascertained; and even the almost endless number of ash-analyses have thereupon given as yet no information. A part of these compounds occur without doubt in plants, in the form in which they are contained in the ash: others are first formed by the process of burning. If we char plants or parts of the same in confined air, and treat the remaining charcoal with water and then with hydrochloric acid, we can withdraw from the charcoal only a part of the salts dissolved therein. The residue we first obtain when the coal by the entrance of the air is fully burnt. Hence is the hypothesis advanced that a part of the salts which occur in the ashes do not occur as such in plants, since their elements immediately are united with carbon, hydrogen, and nitrogen, to form organic compounds. By charring, these elements, as such, must unite again with the remaining carbon, and be first fully oxidized by complete combustion. That the water does not extract all the salts from the coal is sufficiently explained by the known property of the charcoal to withdraw the salts from a watery solution.

plants and animals. Thus, if sulpho-carbonic acid  $\text{CS}_2$  and chlorine be led through a glowing porcelain tube, chloride of sulphur arises, and also a combination which consists of  $\text{C}_2\text{Cl}_4 = (\text{C}_2\text{Cl})\text{Cl}_3$ . If this compound be again led through a glowing tube, it decomposes into chlorine and  $\text{C}_4\text{Cl}_6 = (\text{C}_4\text{Cl}_3)\text{Cl}_3$ . If we treat these bodies with potassa, we obtain 3 atoms chloride of potassium, and  $(\text{C}_4\text{Cl}_3)\text{O}_3$ , or chloracetic acid; and if we let 6 atoms potassium, and 3 atoms  $\text{H}_2\text{O}$  act upon this, we obtain 3 atoms chloride potassium, 3 atoms  $\text{KO}$ , and 1 atom acetic acid  $= (\text{C}_4\text{H}_3)\text{O}_3$ . By the action of chlorine upon sulpho-carbonic acid, under water, we obtain a volatile crystalline body which may be considered as consisting of  $\text{C}_2\text{Cl}_4, 2\text{SO}_2$ . If this compound be overflowed with a solution of potassa, we obtain a potassa salt of an acid which consists of  $\text{C}_2\text{Cl}_3, \text{S}_2\text{O}_5$ , and if this be exposed to the current of a two-paired zinc and coal battery, by the presence of water, the chlorine is gradually replaced by hydrogen, and thus compounds are formed which consist of  $\text{C}_2\text{HCl}_2, \text{S}_2\text{O}_5, \text{C}_2\text{H}_2\text{Cl}, \text{S}_2\text{O}_5$ , and  $\text{C}_2\text{H}_3, \text{S}_2\text{O}_5$ . The substance  $\text{C}_2\text{H}_3$  is methyl, which occurs in combination with oxygen in the oil of the *Gaultheria procumbens*. If, over a mixture of carbon and carbonate of potassa, heated to redness, we lead nitrogen gas, we obtain cyanide of potassium  $\text{K}, \text{NC}_2$ ; cyanogen with hydrogen gives hydrocyanic acid; hydrocyanic acid and water, by alternate decomposition, form formic acid and ammonia. Heated potassium, with oxide of carbon, gives a compound which, by being dissolved in water, forms rhodizionate of potassa, and which then again separates into carbonate and croconate of potassa. Many similar formations of organic compounds out of inorganic material are known.

Formation of organic compounds by decomposition of already existing organic bodies.

As has been repeatedly shown, the individual elements in the organic compounds are not united with each other in accordance with their original affinities, and the combinations owe their greater or less permanency to the greater or less chemical opposition which the organic radicals present to the materials combined with them. If this opposition be considerable, that is, if the affinity of the radical to the materials combined with it is slight, and compounds of distinguished chemical character may arise by the transposition of the individual atoms of the radical, then a great tendency to decomposition is present, and inconsiderable outward circumstances are sufficient to cause it. This inclination to the formation of compounds with marked characters often overpowers the greatest affinities, as is the case in the forming of organic combinations from carbonic acid and water by the vital functions of plants.

If the individual atoms of compound molecules unite in other proportions to form new radicals and combinations, in which the individual components present mutually a greater chemical opposi-



tion, then the formation of these radicals and compounds results from *transposition*. If in the new compounds twice the number of elementary atoms occur as in the original, polymeric or metamer bodies are formed with them. Thus aldehyd  $C_4H_4O_2$  changes into metaldehyd  $C_{12}H_{12}O_6$ , bitter almond oil  $C_{14}H_6O_2$  into benzoin  $C_{28}H_{12}O_4$ . But when the original affinities of the elements overpower the chemical characters of the compounds, decomposition commences by the separation of inorganic matter. The same is complete if all the individual atoms of the compound radicals are led over into inorganic combinations. By this entire decomposition every trace of organization is destroyed. On the other hand, if the decomposition be only partial, if only individual atoms leave the organic radicals, then at once the formation of new radicals and compounds of the same takes place. Thus from ethyl  $C_4H_5$ , by loss of  $H_2$ , acetyl  $C_4H_3$  arises; if from acetyl  $C_2$  departs we obtain methyl  $C_2H_3$ ; again, if methyl lose  $H_2$  it goes over into formyl  $C_2H$ .

Formation of organic compounds by transposition of elements.

Formation of organic compounds by the increase of the primitive affinity of the elements.

The number of new compounds which may arise by partial decomposition is proportionate to the number of single atoms of which the organic radical consists, and the grade of the order to which the compound belongs. Substances which consist only of carbon and hydrogen are generally unchangeable; but if oxygen be united to hydrocarbyls and their original affinity for the elements of the radical be called out by any means, then will this cause the decomposition by forming carbonic acid or water, or both together. In all organic compounds containing oxygen, the atoms of carbon and hydrogen in the radical preponderate over the atoms of oxygen; hence, also, by granting that the oxygen atoms, combined with the radicals, instantaneously receive as many individual atoms of carbon and hydrogen as are necessary to the formation of carbonic acid or carbonic acid and water, there must at once follow a separation of carbon or hydrocarbon. An instantaneous withdrawal of all the oxygen atoms never takes place, for in proportion as single atoms of carbon and hydrogen are absorbed new radicals arise which possess affinity for the yet present oxygen, which by the original affinity of the latter must be again overcome. In combinations of a higher order the decomposibility is mainly dependent upon the opposite chemical properties of the proximate constituents; the stronger these properties appear the firmer are their combinations; but the less their mutual attraction is, the more complex these combinations are, the more do the single atoms seek (mainly through separation of carbonic acid and water, and in the nitrogenous of ammonia also) to unite, forming firmer and less complex compounds. To this class of substances the common constituents of the vegetable kingdom directly belong, and particularly those of the animal organization.

In the compounds containing chlorine, the original affinity of chlorine for the hydrogen of the radicals comes first under consideration. Chlorine decomposes the organic molecule by forming hydrochloric acid. Thus are known proportions of affinity to be considered in the remaining compounds of inorganic chemistry.

Conditions under which decomposition occurs. In only a few cases does decomposition commence when the organic compounds are found in a chemically pure state; if it occur, outward influences are necessary; in the decomposition, either only the elements

which occur in the compound take part, or it takes place by the action of materials which, brought in contact with the organic compounds by their affinity for the constituents of the radicals,

Decomposition without the co-operation of chemically acting matter. cause the decomposition of these latter, forming new combinations; in so doing, the active body either does not enter into the new compounds, or it occasions, by substitution, mainly, the production of *derived radicals*. The decomposition of organic compounds

without the influence of chemically reacting bodies follows:—

- a*, by electrical influence,
- b*, by the influence of heat,
- c*, by fermentation and putrefaction,
- d*, by the vital functions of the animal organism.

If in decomposition, chemically acting matter, as oxygen, takes part simultaneously, the number of the new compounds will be thus increased, and often the decomposition terminates in a complete destruction of the organic constitution. As chemically reacting bodies are to be pointed out besides oxygen, the halogens, and sulphur, strong inorganic acids and bases, ammonia, the strongly positive metals, etc.

Since the organic compounds are not able to obtain their elements by direct union, it is mainly by the results of decomposition that the internal constitution of these compounds can be known. But since this knowledge is the highest scientific aim of organic chemistry, a main question is to investigate with the greatest exactness the products into which organic bodies separate by the above-mentioned influences, and to know, from the similarity or dissimilarity of the phenomena, which heterogeneous bodies present their like or unlike constitution.

A division in the elements of an organic compound often takes place by electrical influence, so that, by the evolution of carbonic acid and hydrogen gas, new and less complex radicals and combinations of the same form. If, for example, we let the current of a six-paired coal-and-zinc battery (whose electrodes are platinum) act upon a most highly concentrated neutral solution of the valerianate of potassa, we thus obtain carbonic

Formation of organic compounds by electrical decomposition of those already existing.

acid, hydrogen gas, a hydrocarbon consisting of  $C_8H_8$ , and an oily portion, whose main constituent is valyl  $C_8H_9$ . The hydrate of valerianic acid  $HO, C_{10}H_9O_3$  separates thence into  $C_8H_9 + 2CO_2 + H$ ; in the same manner butyric acid  $HO, C_8H_7O_3$  separates into  $C_6H_7 + 2CO_2 + H$ , and acetic acid  $HO, C_4H_3O_3$  into  $C_2H_3$  or  $(C_4H_5)H + 2CO_2$  and  $H$ .

A great number of organic compounds go over, at given temperatures, into the gaseous state, without suffering decomposition, whilst by condensing their vapor the original substance may be again obtained. On the contrary, others do not volatilize unchanged, but separate at given temperatures into new products. The volatility of organic substances obtains only at fixed temperatures; many possess the property of volatilizing without decomposition only to the boiling point, and decomposition commences at a slight degree above. Indeed many, whose boiling point is very high, go over, even whilst boiling, into new compounds, so that only a small part volatilize undecomposed, whilst others of lower boiling points may often be heated far above the same without suffering change. But all organic compounds, whether they be volatile at fixed temperatures or not, are decomposed when, with air excluded, they are heated to a temperature varying for the different materials; and this reduction, which an organic body can hardly escape, is denoted by the general term *dry distillation*.

Formation of organic compounds by heat.

Dry distillation.

As is later more plainly shown, in connection with the chemico-physical properties of organic compounds, the volatility or non-volatility of an organic substance depends, first, upon the *elementary constitution*; and, second, upon the *order to which the substance belongs*. Generally, it may be granted that hydrogen limits the volatility, and carbon lessens it; nitrogen also, in many cases, contributes to the volatility, whilst oxygen lessens it. In combinations which belong to a group, or which are placed upon the same grade of constitution, the volatility lessens in proportion as the number of individual atoms increases; thus wood-spirit  $C_2H_4O_2$  boils at  $60^\circ$ , alcohol  $C_4H_6O_2$  at  $78^\circ$ , amyl spirit  $C_{10}H_{12}O_2$  at  $133^\circ$ . Most of the compounds of higher orders are not volatile, as the proximate constituents of plants and animals, many organic acids, the paired bases, etc.

Heat causes the decomposition of organic combinations; since,

1. It tends to cause them to unite and form gaseous compounds, and hence, in non-volatile or not easily volatile substances, to cause a transposition of the constituents in such a manner that combinations are formed more or less volatile.

Action of heat.

2. It tends to destroy the chemical character of the radical by increasing its original affinities for the substances combined therewith.



The products which are formed by the decomposing influence of heat are varied:—

1. By the constitution of the organic substance; and,
2. By the intensity of the heat to which they are subjected.

Combinations which consist only of carbon and hydrogen, in

Decomposition  
of compounds  
consisting of  
carbon and  
hydrogen.

small atomic number, are most generally gaseous at common temperature; the more complex are either fluid or solid. If these latter be exposed to the lowest temperature necessary to decomposition, several of them separate into less complex compounds, the most of which are fluid, in which, however, the absolute proportion of the carbon and hydrogen atoms suffers no change; more strongly heated, frequently a division of the elements takes place, in such a manner that highly hydrogenous compounds of simpler constitution escape, whilst those richer in carbon remain. But if we suddenly apply to these compounds a violent glowing heat, a separation of carbon always takes place, accompanied by evolution of gases abounding in hydrogen of simple constitution, as  $C_2H_4$ ,  $C_2H_2$ . The products formed at a lower temperature suffer also the same decomposition when they are suddenly subjected to intense heat—hydrogen being always separated; thus,  $C_4H_4$  separates, according to the temperature, either into  $C_2H_4$  and  $H_2$ , or into  $C_2$  and  $H_4$ . If organic bodies containing oxygen be subjected

Decomposition  
of oxygenous  
bodies.

to the influence of heat, besides the above-mentioned circumstances, the original affinity of oxygen for the elements of the radical comes into view. The simpler the constitution of the compounds is, the simpler also is the process of decomposition, if the temperature be slowly raised to the point at which the reduction commences, and be held steady until at the given temperature products escape; thus, meconic acid  $C_7H_2O_7$  separates at  $200^\circ$  into komeinic acid  $C_6H_2O_5$ , and into  $CO_2$ ; and these by higher temperature into pyromeconic acid  $C_5H_2O_3$ , and into  $CO_2$ . In the first action, more compounds are formed, rich in oxygen; but since oxygen always escapes in the formation of carbonic acid and water, or both together, simultaneously, new combinations are formed, which, being transient, escape, and thereby avoid the farther action of heat. Volatile organic acids united to bases are decomposed by heat in the same manner as the non-volatile. Thus, two atoms of acetic acid  $C_8H_6O_6$  separate into acetone  $C_6H_6O_2$ , and into  $2CO_2$ . The hydrate of benzoic acid  $C_{14}H_6O_4$ , by being heated with hydrate of lime separates into benzin  $C_{12}H_6$  and  $2CO_2$ ; camphor  $C_{10}H_8O$ , by being distilled with anhydrous phosphoric acid, gives camphin  $C_9H_7$  and  $HO$ . Two atoms of mucic acid  $C_{12}H_8O_{14}$ , by being heated, separate into pyromucic acid  $C_{10}H_{15}O_5 + 2CO_2 + 3HO$ . Acetone as well as pyromucic acid contains a larger number of carbon atoms than acetic acid and mucic acid; but, as will be given later, acetone is a compound

$=C_2H_3\cdot(C_4H_3)O_2$ , and pyromucic acid  $=C_4H\cdot(C_6H_4)O_5$ . It is seldom the case that in decomposition by heat compounds of more complicated constitution are obtained. When these compounds are suddenly subjected to a glowing heat they form a great number of new products, constantly evolving gases. The connection between the products of decomposition and the original substance will hereafter be more fully explained in the special grouping of the organic radicals and their combinations. Here must be briefly noticed the appearances only observed in peculiar dry distillation.

If the non-volatile compounds of the higher order, as gum, woody fibrine, sugar, be exposed in a distilling apparatus to a constantly increasing heat, those which melt

Dry distillation.

in a high temperature first become fluid and then boil. Those not fusible, as wood, to which most analyses principally relate, are colored brown, and have a peculiar unpleasant smell. From the commencement to the termination of the operation gaseous products escape which are continually changing. In materials abounding in oxygen, as wood, gum, etc., much

Gaseous products.

carbonic acid is evolved at first, and, later, carbonic oxide; thus, whilst oxygen acts upon the radicals, and oxidizes a part of the carbon atoms, new radicals form, which either escape of themselves or unite with the yet present oxygen forming volatile oxides. In proportion as carbonic acid and carbonic oxide diminish gases escape, consisting of carbon and hydrogen; in wood and similar compounds these gases are poor in elayl gas  $C_4H_4$ , and other gases absorbed by chlorine, and contain, on the contrary, much marsh gas  $C_2H_4$ . If the temperature be constantly raised, and the greater part of the oxygen escape, new compounds continually distil over, which either contain no oxygen, or only a little. If the sides of the apparatus are placed in a strong glowing heat, the carbonaceous gases first separate into carbon and hydro-methyl, and finally into carbon and hydrogen. Combinations poor in oxygen and rich in hydrogen, as fats, resins, and the fluid products which are formed with the gases in dry distillation, when let fall drop by drop into a glowing cylinder filled with stones, are in a moment decomposed. If the apparatus be but feebly glowing, the gaseous mixture which escapes is rich in carbon; it burns with a clearer flame, and, therefore, bad kinds of oil, pitch oil, tar, etc., are used for gas-light. The gas obtained by dry distillation of hard coal, and particularly of common charcoal, if not produced in too high a temperature, is rich in carbon. Indeed, if the heat be very high, approaching to white heat, the gases formed first separate into carbon and hydrogen.

In highly oxygenous bodies, simultaneously with the gaseous products, a nearly colorless fluid first goes

Fluid products.

over, which is almost destitute of water; later, this fluid is colored by the formation of a thick yellow smoke; by raising the temperature an oily fluid appears, becoming ever darker

and thicker, until it is nearly black, and of such a consistence as scarcely to be able to flow down the sides of the apparatus. The fluid compounds, which in the commencement of the dry distillation of wood and similar compounds are formed, together with water in which they are dissolved, are oxygenous and volatile; they consist principally of acetic acid, spirit of wood, acetate of methyl, xylit, mesit, etc.; the offensive brown, oily, and tar-like distillate, which is formed later, is a mixture of carboniferous and hydrogenous compounds; in them occur creosote, kapnomar, picamar, etc.; in substances containing little oxygen, as in the distillation of resin, hard coal, and oils, interesting products are formed, consisting of carbon and hydrogen, as salicyl, naphthalin, retinyl, retinaphtha. Finally, gases and volatile products are no longer evolved, and the process is thus ended. As residue, carbon is found; it appears as a black porous mass.

Organic charcoal.

If the substance before and during the decomposition is not fusible—as wood, the charcoal retains the form of the substance from which it is obtained; in the other case it appears as a swollen, spongy mass, like the charcoal obtained by the dry distillation of sugar. If the vapor of volatile hydrogenous compounds be led through a tube heated to whiteness, the charcoal is separated in the form of a fine powder. In large quantities wood, hard coal (coke), and peat, are used especially for the production of charcoal; brown coal is but seldom used. The amount of charcoal from wood is so much the greater, the more oxygen unites with hydrogen, and the more completely the latter is freed, before the decomposition, from hygroscopic water, as also the slower the distillation proceeds; by being slowly charred from air-dried wood, which contains from 16 to 20 per cent. water, this amounts to from 25 to 27 per cent.; by being quickly heated we seldom obtain more than 15 per cent. In the latter case, those portions of wood which lie nearest the sides of the distilling apparatus at once decompose, and the separated carbon is in a glowing state, whilst that lying in the middle, just attains the temperature at which the hygroscopic water evaporates. The aqueous vapor which forms is decomposed by the glowing coal, a part of which is thereby removed by the formation of oxide of carbon. (Charring in entire, or half-closed space—kiln charring.)

All nitrogenous compounds, if at the same time they contain hydrogen, give by dry distillation ammonia. In the decomposition of neutral substances of this class, with large atomic weights, as the albumen and fibrin of horn, claws, etc., essentially the same phenomena occur as in the dry distillation of the non-nitrogenous. If this decomposition be undertaken without the action of foreign matter, each time a considerable quantity of carbonate of ammonia is evolved at the commencement of the operation; moreover, other

Decomposition of nitrogenous bodies.



volatile organic bases are formed, agreeing in chemical relation with ammonia. Since these compounds all melt in a higher temperature there remains as residue a considerable quantity of porous nitrogenous charcoal. If the above-mentioned substances, mingled with strong bases, as potassa, be subjected to dry distillation, and towards the end of the operation the heat be raised to intense redness, cyanmetal  $K,NC_2$  is formed. If we heat this substance to redness, with an excess of hydrate of potassa, all the nitrogen escapes as ammonia.

Since, in the organic compounds, the atoms of oxygen are insufficient to the complete oxidation of the carbon and hydrogen atoms of the radicals, it follows that to this end the yet wanting oxygen must enter from without. The fewer the individual atoms of carbon and hydrogen occurring in the radicals, and the more numerous the atoms of oxygen combined therewith, the less the oxygen from without, necessary to a complete oxidation or combustion. The products may be only water and carbonic acid. If the compounds contain more nitrogen, it escapes as gas. But the more complex the organic radical is, the smaller the number of oxygen atoms combined with it—the less can a simultaneous combustion of all the carbon and hydrogen atoms occur. Hence, in most cases, the phenomena of dry distillation precede combustion. In the burning of such compounds, at first only the upper surface of the substance comes in contact with the oxygen; the inner portions do not at the same time meet with any, but by the heat of the burning portions, as in a retort, they are subjected to dry distillation; now, as the products of distillation within the mass break forth, and in a glowing state come in contact with the air, they kindle into a flame. By the burning of these volatile products, the oxygen of the air is absorbed, and thus its entrance to the separated charcoal is hindered. This can only burn when no more volatile matter escapes. If there be oxygen present, sufficient for the products of distillation, which may be afforded by a strong draft of air, they are thus completely burnt to carbonic acid and water. In most arrangements for fire this is not quick enough, and hence a part of the products of distillation surrounded by nitrogen, carbonic acid, and hydrogen gas, escape from the flames; they become condensed in the cold air, and form the smoke which is deposited as soot in the channel through which the draft goes (evolution of heat and light by burning).

In the same manner as by oxygen gas, complete oxidation can be effected by inorganic oxides, which easily yield their oxygen, as nitric acid, chromic acid, and their salts, and above all, by those inorganic compounds in which the oxygen is not bound by great affinity. Indeed, the oxides which, when heated by themselves, evolve no oxygen, as oxide of copper, are reduced, when they are

Dry distillation of organic compounds by simultaneous action of oxygen. Combustion.

mixed in large quantities with organic matter and subjected to a high temperature, carbonic acid and water being formed. Upon this is founded *the principle of elementary organic analysis*.

As by heat, so also by other yet partially known influences, the primitive affinities between the elements of an organic substance may be called out, and thus decomposition be caused by the separation of inorganic, and the formation of new organic materials.

If this decomposition take place even at common temperature, it is called putrefaction, or fermentation. By putrefaction, however, is understood chiefly the decomposition of the nitrogenous and by fermentation that of the non-nitrogenous substances. The name of voluntary decomposition is given to it.

All combinations which consist alone of carbon and hydrogen, are not subject to voluntary decomposition. The degree of decomposibility of the organic oxides, is often dependent upon their solubility in water, doubtless because their constituents frequently take part in the formation of new compounds. Thus, the combinations insoluble in water, as the volatile oils, the resins, the fatty acids, and also those not easily soluble in water, as benzoic, cuminic, and camphoric acid, and generally those compounds possessing little oxygen, all show great durability; whilst those acids rich in oxygen, easily soluble in water, as tartaric acid, malic, and citric acid, etc., are greatly inclined to voluntary decomposition. It is frequently, therefore, the combinations of a higher order, particularly the common compounds of the vegetable kingdom, as starch, gum, sugar, as well as those of the animal organization, as albumin, fibrin, and casein, in their fresh state, or the so-called protein compounds, and the glutinous and cartilaginous tissues, whose proximate constituents are combined only by weak affinity, which are worthy of mention; and the inclination to decomposition increases with the number of elements, and of the individual atoms which constitute the compound. Decomposition is particularly strong in the combinations of the animal body, and of assimilated vegetable matter. Very tenacious nitrogenous compounds, even cohering protein matter—as hair, are not subject to putrefaction. Decomposition generally begins when the above-mentioned substances, either dissolved in water, or fully saturated therewith, are subjected to a temperature of from 10 to 30°. Air is necessary to

the commencement of putrefaction, but when once it is begun, it proceeds rapidly, even if the air be completely withheld. The compounds which easily putrefy, contain mostly a small quantity of sulphur and phosphorus. Putrefaction consists in this, that nitrogen, sulphur, and phosphorus, enter into combination with a portion of the hydrogen of the organic substance, whilst the oxygen unites with one part of carbon. Putrefaction is at once known by an unpleasant odor which arises,

particularly by the evaporation of the hydrogen compounds, and becomes, as the process advances, insupportable. But since the oxygen is insufficient for the entire oxidation of the carbon, and of the hydrogen, which is not used in forming hydrogen compounds, an evolution of hydrocarbon and of pure hydrogen gas takes place, whilst the carbonic acid is almost entirely absorbed by the produced ammonia. In the different stages of putrefaction arise without doubt, as in dry distillation, a great number of new organic compounds, whose properties and constitution are as yet entirely unknown; in some stages, the products of decomposition have poisonous properties. Putrefaction is generally accompanied by the production of infusoria; indeed, it is not improbable that these infusoria are the middle member of the entire decomposition.

The common non-nitrogenous compounds of the vegetable kingdom, when pure, are much less liable to voluntary decomposition. A solution of pure sugar suffers for a long time no change; even nitrogenous bodies, as urea, behave in like manner, but if their aqueous solutions be brought in contact with the easily decomposable nitrogenous combinations, particularly after these have commenced to putrefy, under conditions otherwise favorable, fermentation very quickly begins. According to the condition and degree of change in which it occurs, the same nitrogenous substance can convert the same non-nitrogenous substance into different products. Fresh animal membrane carefully cleansed, and suffering no decomposition, shows no action upon sugar, gum, or starch; but if it be attacked by decay, and then be brought into contact with a solution of sugar at the different points of time of its own change, the sugar separates soon into lactic acid and water, into mannit and slime, into butyric acid evolving hydrogen gas, also into alcohol and carbonic acid. The nitrogenous substance attacked by decomposition which causes the fermentation of the others is called a *ferment*. Every body that is decomposed by the action of ferment is called *fermentable*. The ferment loses its power of causing fermentation the moment its own decomposition is ended; also, it acts so long only as it is putrefying. According to the chief products which are formed by fermentation, we distinguish vinous fermentation, lactic acid fermentation, butyric acid fermentation, etc.

The phenomena presented by vinous fermentation, are, in their detail, most accurately known. This fermentation consists in the separation of grape, or fruit sugar, into carbonic acid and alcohol. 1 atom of sugar  $C_{12}H_{22}O_{12}$ , separates into 2 atoms of alcohol  $C_2H_5O$ , and 4 atoms carbonic acid  $C_4O_2$ . Indeed, since starch, cane sugar and milk sugar are easily converted into fruit and grape sugar, they can be used in the manufacture of alcohol. In the natural sugar saps, as in the ripe grape juice, the principal constituents are fruit—and grape sugar on the



one hand, and a nitrogenous "protein" compound on the other. So long as the sap is inclosed in the fruit-cells it suffers no change, nor when it is pressed out in air entirely free from oxygen; but if only a little air comes in contact with the pure sap, it clouds and thickens it in a very short time at a temperature of from 10 to 15°, and simultaneously the evolution of carbonic acid and the formation of alcohol begin. But this decomposition does not take place, if the air be previously led through a heated tube. So long as undecomposed sugar is present, the fluid is in constant motion, and becomes clouded as the fermentation progresses. When that is ended, that is, when the sugar is entirely separated into alcohol and carbonic acid, the fermented fluid is clarified by the deposition of a grayish white mass, which possesses in a remarkable degree the property of fermenting new quantities of sugar without the presence of the air; if the sugar dissolved in from 6 to 12 or more parts of water, be exposed to a temperature of 10 to 15°. From

Yeast. 2 to 3 parts of this substance called yeast, possesses the property of decomposing 100 parts sugar.

Thus, a given quantity of yeast can only cause a given quantity of sugar to ferment; if more of the latter be present, after the decomposition, the excess remains unchanged in the fluid. The deposition thus formed has no power of causing fermentation in a

Decomposed yeast. solution of sugar, and is called *decomposed yeast*. In a pure solution of sugar, yeast is never formed; the material whence it arises is nitrogenous. If to a fermenting fluid we add albumen, or similar protein compounds, we can thus increase very perceptibly the quantity of yeast. Accord-

Nature of yeast. ant microscopic investigations have proved, that the undecomposed yeast is a plant (yeast fungus), consisting of simple cells, in size at most but 0.01 m.m.,

which nourish themselves, increasing independently, and consist of a non-nitrogenous sheath, and a nitrogenous substance. In decomposed yeast, the cells are broken up, and the inner substance removed, whilst the insoluble sheath remains. So long as this substance is putrefying, so long the fermentation of the sugar continues, that being consequent upon the direct contact of the yeast-cells with the sugar solution. If by rubbing we destroy the cells, fermentation does not commence until new cells are formed.

Putrefaction, as well as fermentation, may be prevented by various means, or if already begun may be arrested in its details. Thus, the power to produce fermentation possessed by yeast, like the putrefying of nitrogenous bodies, is sometimes entirely destroyed, sometimes hindered: 1. By entire desiccation at 100°, also by continued boiling in water, by which the protein substances go over into an insoluble coagulated state; 2. By complete exclusion of air, for, as has been already remarked, air or oxygen gas

Destruction of the power of producing fermentation.

is always necessary to the commencement of putrefaction as well as to the formation of yeast; the exclusion of air is, hence, an excellent means of preventing putrefaction. The same end is attained if the substances in closed air-tight vessels are slowly heated (meat may be preserved many weeks in boiled water, if the surface of the water be covered with a layer of oil); 3. By a *low temperature*; at or below  $0^{\circ}$ , neither putrefaction nor fermentation takes place; 4, as they either absorb the water necessary to putrefaction from the substances, or form chemical compounds in which the inclination to putrefaction is destroyed. Alcohol of 70 to 80 per cent. (preservation of anatomical preparations), saltpetre, common salt, act without doubt by absorption of water. As chemically acting can be considered strong mineral acids, sublimes, salts of copper, as blue vitriol, many organic compounds, as creosote and others similar, formed by dry distillation (wood vinegar), particularly tannin, for they form with nitrogenous bodies insoluble compounds; in similar manner act flowers of sulphur, sulphurous acid and its salts, sulphurous volatile oils, as mustard oil, chloride of lime, etc. When non-nitrogenous compounds occur mingled with nitrogenous, they can be protected from decomposition if the nitrogenous compounds are removed as quickly as possible. (Production of sugar from sap, washing wood with lye.) As sugar separates in vinous fermentation into carbonic acid and alcohol, so the non-nitrogenous compounds, as starch, sugar, gum if they be brought into contact with different ferments, separate according to the temperature, into lactic or butyric acid—always in the latter case hydrogen gas is evolved. Animal casein, already attacked by putridity, serves as a ferment. This decomposition appears to be consequent upon the existence of certain fungi.

Lactic acid and butyric acid fermentation.

Pure urea behaves in aqueous solution like sugar, it suffers no change. Fresh urine, in which animal mucus is found, together with urea, putrefies slowly in a perfectly clean vessel; but if some yeast be added to the urine putrefaction commences in a few days. If we let urine putrefy without the addition of yeast, during the process a ferment is formed which is deposited as a white powder, it possesses the property of completely decomposing a large quantity of fresh urine within twenty-four hours at a temperature of  $12$  to  $16^{\circ}$ . Urea separates by putrefaction into carbonate of ammonia, simultaneously with the decomposition of water.

Fermentation of urea.

In vinous fermentation, the ferment only acts so long as it suffers decomposition itself; this fermentation, therefore, consists in simultaneous decomposition of nitrogenous and non-nitrogenous substances. In many cases the nitrogenous substance acts as a ferment without having previously suffered decomposition. If to

Fermentation of bitter almond oil, salicin, and mustard oil.

a solution of amygdalin, a freshly prepared solution of emulsin or an emulsion of sweet almonds be added, it separates at once into oil of bitter almonds, hydrocyanic acid, and sugar. Thus salicin, by a similar action, is decomposed into saligenin and sugar. Myronic acid, which occurs in black mustard, separates, by the influence of a nitrogenous, emulsion-like substance occurring in mustard, into etheric mustard oil. Indeed, even a solution of sugar by contact with paper, straw, or pulverized coal can be led into the butyric acid fermentation.

Whilst, by the above-mentioned phenomena of fermentation and putrefaction, a body whose constitution is that of a higher order separates into substances less complex, neutral organic substances certainly have the property to lead organic compounds over into others equally or even more complex in their constitution. Thus, in barley malt occurs a substance, *diastase*, a small quantity of which can lead over a large quantity of starch—by the presence of water and at a temperature of  $40^{\circ}$  to  $50^{\circ}$ , first into dextrin, which is isomeric with starch, and then by taking the elements of 2 at. water into sugar; but if the solution of diastase be heated to boiling, it completely loses its efficiency. Dilute acids act in the same manner as diastase; 1 part sulphuric acid dissolved in 400 parts water changes in the heat in a few hours from 30 to 40 parts starch into sugar, without forming a compound itself or suffering a change. A small quantity of rennet coagulates a large quantity of casein.

Hitherto no satisfactory explanation has been given of the influence exerted by the ferments upon substances during fermentation. Liebig sought the cause of the phenomena of fermentation in the property of decomposing bodies of inducing the same action in another substance with which they are brought in contact; that is, to make them capable of suffering the same change. From the fact that yeast is organic, others have ventured to believe that its vitality calls out the primitive affinities in fermentable bodies, and thus controls their decomposition. The germs of fungi must be contained in the air; hence, if the air which is necessary to the commencement of putrefaction be led through a tube, the germs are thus destroyed, and putrefaction does not take place. Since in the phenomena of fermentation no chemical action of the ferment is perceptible, and fermentation follows only upon the immediate contact of the solution of sugar with the yeast, and since, in the action of emulsin upon amygdalin, and of diastase upon starch, no previous decomposition of the ferment can be received, therefore Berzelius and Mitscherlich compare the action of ferments to that of platinum upon a mixture of hydrogen and oxygen gas. According to Berzelius, the ferment acts catalytically upon the

Action of diastase upon starch.

Theories of fermentation.



elements of sugar, causing them to separate into carbonic acid and alcohol. According to Mitscherlich, the upper surface of certain bodies has the power by immediate contact to cause decomposition, and to form combinations in other substances; he calls these "contact substances." But these explanations are not altogether satisfactory. Since nitrogenous bodies do not putrefy at or below  $0^{\circ}$ , it may be supposed that attaining to a gentle heat calls forth the primitive affinity of oxygen for the elements of the radicals, and thereby causes decomposition.

The first cause of the phenomena of fermentation is, that the elements of putrefiable and fermentable bodies are united together by a weak affinity only, and not by primitive affinity; trifling causes are sufficient to call the latter forth; hence the ferments act like heat, and their mode of action is as little known to us as is that of heat. Every fermentation or putrefaction is accompanied by the evolution of heat. In fermentation, when the mass is considerable, the temperature is raised from  $5$  to  $8^{\circ}$ . Hence, the heat which becomes free is not inconsiderable, since the capacity of water for heat is great; and besides, in the formation of carbonic acid gas, a part becomes latent. This heat is brought forth by the action of the oxygen of sugar upon the organic radicals; and whilst this oxygen, with one part of the carbon atoms, forms carbonic acid, nearly as much heat must become free as in direct combustion. If, in the decomposition of organic compounds, no inorganic are formed, but the former only separate into new organic bodies of a lower order, either none or only a weak evolution of heat is perceptible.

Evolution of heat by fermentation and putrefaction.

Fermentation and putrefaction, under the influence of the oxygen of the air, agree in their final results with the combustion of organic bodies. Putrefying matters gradually absorb as much oxygen as is necessary to the complete oxidation of their carbon and hydrogen atoms, only the process of oxidation proceeds slower as in combustion proper, and, before it is ended, a series of new compounds is formed, many of which are distinguished by their great durability, and to a certain degree oppose the action of oxygen. The finer the putrefying body is divided, the higher the temperature, and the freer the air can act upon that body, the more rapidly decomposition advances. This decomposition, which is called *corruption*, *mouldering*, and also *slow burning*, is always accompanied by evolution of heat, although seldom by that of light; sometimes the heat is raised to such a degree that a violent combustion ensues. Corrupt nitrogenous compounds form ammonia in the commencement by the putrefying process; in complete oxidation the nitrogen is set free as gas; if at the same time strong bases are present, the nitrogen is oxidized by

Fermentation and putrefaction under the influence of the oxygen of the air.

its predisposing affinity forming nitric acid. Non-nitrogenous compounds, attacked by decay, appear under certain conditions to absorb nitrogen from the air, forming at the same time ammonia, or, if strong bases be present, nitrous or nitric acid.

Many organic compounds in their pure state, suffer no change in the air; but, if they be exposed to the air, together with ferments, a partial oxidation often commences. Alcohol mixed with yeast, exposed to the action of oxygen, goes over by partial oxidation of the hydrogen into aldehyd, and then, by the oxidation of this substance, into acetic acid; from  $C_4H_6O_2$  is first  $C_4H_4O_2$ , and then  $C_4H_4O_4$ . Finely divided platinum acts like yeast.

Decomposition  
and formation  
of organic bod-  
ies by vital  
action of ani-  
mal organiza-  
tion.

Animals, particularly the more highly organized, do not possess, like plants, the property of preparing the compounds necessary to their existence from inorganic matter, as carbonic acid, water, and ammonia. All substances which they need as nourishment must be presented to them in an organized form, as they occur in plants. It is especially those belonging to

the class of protein compounds which must be considered particularly as nourishment. These agree in their essential properties with the principal constituents of the animal body, and are distinguished from the latter only by containing less oxygen. But, in proportion as the animal receives new food, that previously taken and used for the growth of the body is removed; and since all parts which are separated depart from the received food, and are no longer of service as nourishment, it is self-evident that, in the animal body, a continual decomposition of the food received must take place. As is known, all nutrition takes place through the blood; the food must hence, if it serve for nutrition, be converted into blood. This conversion is consequent upon the act of digestion, which commences when the food is mixed with the saliva in the mouth, and terminates when it is fully assimilated and poured in with the venous blood on its returning course to the heart. In order that it be actual nutriment, it must absorb more oxygen, which it does in the lungs. Out of the blood, reparation is made for the waste caused by the vital functions, whilst at the same time this waste matter is quickly removed by various organs. Here we see that, in the animal organization, two processes always go on together. One is the process of *assimilation*, which may be compared to the conversion of starch into sugar, under the influence of diastase; the other is the process of *decomposition*, or *excretion*, and is classed with putrefaction and fermentation. The whole is denoted by change of matter, and in the right proportion of both lies the normal state of the vital powers. The higher compounds which have served as nutriment, separate as in putrefaction, in consequence of the reaction of oxygen, combined with carbon and hydrogen atoms, into carbonic acid, water, and lower organic com-

pounds, as urea, uric acid, etc. But this process of decomposition must necessarily be accompanied by evolution of heat, as in fermentation, and this is the source of *animal heat*; since this decomposition goes on uninterruptedly in all parts of the animal body simultaneously, so must also the evolution of heat follow in every part of the animal organization; great abnormal chemical action in particular parts must necessarily be attended by great evolution of heat in the same, for it is not consequent upon the direct influence of the oxygen respired upon the organic matter. From what has been said, it follows that firm organic compounds, and those containing much nitrogen, are not adapted for food.

Chemically acting substances, as oxygen, the halogens, strong acids and bases, either are directly combined with organic bodies, or they effect a decomposition of the same at ordinary or lower temperature, by their chemical affinities. Frequently, this consists in the transposition of the atoms of an organic substance in such a manner, that basic or acid combinations are formed, which unite themselves with the acting materials, or these latter combine with the proximate or ultimate constituents of the organic substance. Many organic compounds, especially those consisting of carbon and hydrogen, as also many poor in oxygen, are distinguished by their great durability, whilst others, especially compounds of a higher order, by the action of inorganic reagents, either separate into their proximate constituents, one of which combines with them, or they suffer by strong acids and bases such a transposition that chemically opposite compounds are formed, which unite with the acting acid or base. Often, indeed, it is doubtful, on account of the ease with which many organic bodies decompose, if the products which are thus obtained are actually the proximate constituents of the organic compounds, or if the decomposition of the radicals has not taken place.

According to the original affinities of the acting bodies for the individual atoms of the organic combinations, the products of the decomposition of the same substance must be various. By the action of *oxygen*, is seen its great attraction for carbon and hydrogen. If from the hydrocarbyls single atoms of carbon or hydrogen, or both together, be withdrawn, new radicals thus arise, some containing carbon, some hydrogen in abundance; which radicals either remain combined with the substances that were united with the original radicals, or they oxidize immediately at the expense of another part of oxygen; here belong the phenomena of decay. The *halogens* act in many cases similarly to oxygen; they decompose the organic radical,

*Animal heat.*

Formation of organic compounds by the decomposition of those already existing, by means of chemically reacting matter.

Action of oxygen.

forming hydrogen acids, and radicals containing little hydrogen, which enter into combinations with the halogens; thus, oxide of ethyl  $C_4H_5O$ , brought in contact with chlorine, goes over first into oxide of acetyl  $C_4H_3O$  by withdrawal of  $H_2$ . If oxide of acetyl takes  $Cl_2$ , thus is obtained oxychloride of acetyl  $C_4H_3 \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$ .

Action of oxidizing compounds.

Oxidizing compounds, as nitric acid, chromic acid, hypermanganic acid, the superoxides, oxide of silver, oxide of mercury, etc., likewise several metal salts, cause in few cases only a complete oxidation of the whole compound; they mostly cause only a partial decomposition, forming carbonic acid and water, as well as new radicals which often unite with the acting substances. The easier oxidizing bodies yield oxygen, the more rapidly and completely does the oxidation of the organic substance follow. The products which are formed depend farther upon the degree of concentration in which the oxidizing bodies act, and upon the solubility of the organic substance, etc.

Action of reducing matters.

If organic oxides come in contact with deoxidizing bodies, as with hydrogen, hydrosulphuric acid, potassium, zinc, etc., they are often entirely or partially reduced, without the radicals suffering a change. If we let potassium act upon hydrates, the hydrate water is decomposed, and we obtain combinations of the oxides with potassa; thus anhydrous alcohol brought in contact with potassium gives ethyloxyd-potassa  $(C_4H_5)O, HO + K = KO(C_4H_5)O + H$ . In nitrogenous bodies potassium often causes the formation of cyanogen.

Organic chlorine compounds are similarly decomposed, forming hydrochloric acid, chloride of potassium, etc., as in most cases the same reactions are observed in the corresponding inorganic combinations. By the influence of chemically acting substances upon organic bodies, new combinations arise with distinguished acid or basic properties; thus the changes generally proceed more quickly when bodies are present which possess opposite chemical properties from those which are formed; thus alcohol, heated with water, suffers no change; but if at the same time potassa be present, acetate of potassa is formed, whilst hydrogen gas is evolved.

Different from the decompositions by chemically reacting substances are those in consequence of which derived radicals are formed by substitution from the primary. Since in this connection the primary radicals behave differently, therefore, in the following grouping of the organic radicals, the details of the transition of the primary into the derived radicals must be given with each group.



## CONSTITUTION OF THE ORGANIC RADICALS.

## DIFFERENT GROUPS.

It has been repeatedly remarked that an organic molecule which plays the part of a radical may consist of many or few simple atoms, and is to be viewed in its combinations as an indivisible whole. This is the explanation of the reactions which occur when the organic compounds are brought in mutual reaction with other materials. Acetyl  $C_4H_3$  is a radical because this complex atom forms with  $O_3, Cl_3, Br_3, I_3$  a series of equivalent compounds; if we treat  $(C_4H_3)Cl_3$  with potassa, we obtain chloride of potassium and acetate of potassa  $KO(C_4H_3)O_3$ ; ethyl  $C_4H_5$  is also a radical, for it combines with  $O, S, Cl, Br$ , etc., in the same proportions as hydrogen or a positive metal; for the same reason chloracetyl  $C_4Cl_3$  is also a radical, for it gives the same combinations as acetyl  $C_4H_3$ , etc. But another question is, how are the individual elements and atoms united together in an organic molecule or radical? Since no direct observations are possible, the answer to this question can only be theoretic; and the more so, since many equally probable and current opinions may be formed. Indeed, people will always give that theory the preference which can combine the known facts most consistently in a common whole, with the fewest suppositions. Often when we have succeeded in casting a glance into the depths of nature, we are astonished at the simplicity of the means used for the attainment of the most different ends; and it may be asserted without exaggeration, that the more complicated the suppositions are which support a theory, the farther is it removed from the truth. Since the organic compounds cannot be produced directly from their elements, the similarity or difference of their internal constitution is mostly to be known only from the products of decomposition into which different bodies separate by the action of one and the same substance. Benzin ( $C_{12}H_5$ )H and phenole ( $C_{12}H_5$ )O, HO have according to these formulæ the same constitution; if we treat both bodies with nitric acid, we obtain quite different products. Thus, phenole gives with chlorate of potassa and concentrated hydrochloric acid chloranil as a final product; benzin gives no trace of this substance. Benzoic and salicylous acid both correspond to the same formula  $HO, C_{14}H_5O_3$ ; an alkaline solution of benzoic acid suffers no change in the air. On the contrary salicylous acid dissolved in potassa absorbs oxygen and separates into acetic acid and melanic acid. By the action of chlorine upon formate of methyl  $C_4H_4O_4$  as a final product we obtain  $C_4Cl_4O_4$ ; if

Constitution of  
the organic ra-  
dicals.



we bring this compound together with wood spirit, there arises a compound  $C_4H_3ClO_4$ . Thus, acetate of ethyl  $C_8H_8O_4$  goes over finally into  $C_8Cl_8O_4$ ; if this body be brought with potassa, we obtain  $C_8Cl_6O_6$ . It is for theory to give the reason why in the former case 3 atoms of chlorine leave  $C_4Cl_4O_4$ , and the replacement by hydrogen follows; whilst in the latter  $Cl_2$  is substituted by  $O_2$ .

By far the greater number of organic compounds are to be traced back to radicals which consist of carbon and hydrogen, and were called above, *Hydrocarbyls*. By an accurate observation and comparison of these in every aspect which they present, it is found that they belong to different groups, and that those of each group mostly form an ascending series in which each successive member contains the same number of carbon and hydrogen atoms as the preceding. But whilst the radicals of one group, in their combining proportions, are allied to hydrogen and the positive metals, those of another agree in this relation with the negative.

In all the radicals of the hydrocarbyls may be distinguished: 1. *the Active Element or Molecule*; and 2. *the Ascending Passive Component*, by which the individual members of a group are formed. In all Organic Radicals which have a Positive character, the Active Part is  $H$ ; in the Negative  $C_2H$ . The Ascending passive member of the Component is always  $C_2H_2$ . All radicals which appear as simple combinations of the components  $C_2H_2$  with the active  $H$  or  $C_2H$ , form the class of the *Hydroisocarbyls*. But if between the ascending  $C_2H_2$  and the active  $H$  or  $C_2H$  another molecule of carbon atoms enters  $=C_2, C_4, C_6, C_8$ , which may be considered as *Nucleus*, we thus obtain the class of *Hydropolycarbyls*.

## FIRST CLASS.

### HYDROISOCARBYLS.

To the radicals of the hydroisocarbyls belong:—

- The *Methyl Group*; component  $C_2H_2$ , active part  $H=C_2H_3$ .
- The *Formyl Group*; “  $C_2H_2$ , “ “  $C_2H=C_4H_3$ .

The radicals which form the basis of wood spirit, Methyl group. alcohol, spirit of amyl, etc., form an ascending series which correspond to the formulæ  $C_2H_3, C_4H_5, C_6H_7, C_8H_9, C_{10}H_{11}$ . . . .  $C_{60}H_{61}$ . These radicals all unite in the same atomic proportions with  $H, O, S, Se, Cl, Br, I$ , forming equivalent compounds which possess the same chemical character. The difference which they present in physical relation, is alone dependent upon the difference of their carbon and hydrogen atoms. In all, the hydrogen

atoms exceed the carbon by one, whilst the single members of the group differ from each other by a plus or minus of  $C_2H_2$ . The first member of the series is methyl  $C_2H_3$ ; if we withdraw  $C_2H_2$  there remains H. These radicals, hence, appear as combinations of H with  $C_2H_2, 2C_2H_2, 3C_2H_2$  . . . . . The atom of hydrogen is the ground radical—the active element, and, in fact, the combining series of these radicals entirely correspond to that of hydrogen, not alone in the compounds with the above-mentioned negative elements, but also in those with N, P, Ar, St. Like hydrogen, methyl unites with the above-named elements in many proportions, forming strong basic bodies. Thus, as  $NO_5$  by loss of  $O, O_2, O_3, O_4$ , goes over gradually into  $NO_4, NO_3, NO_2, NO$ , so we obtain the lower members from the higher by the withdrawal from the latter of  $C_2H_2, 2C_2H_2, 3C_2H_2$  . . . Thus, ethyl  $C_4H_5$ , by loss of  $C_2H_2$ , goes over into methyl. All radicals of this group give, with 1 atom of oxygen, oxides; which, like the inorganic, unite with the acids to form salt-like compounds. The constitution of these radicals may, therefore, be expressed by the formulæ:—

*Methyl* =  $C_2H_2, H$ ; *Ethyl* =  $2C_2H_2, H$ ; *Amyl* =  $5C_2H_2, H$ , etc.

Therefore, in these the component and active part must be thought to combine and form a simple organic molecule. All organic radicals correspond, in their gaseous state, to 2 volumes, equally, if  $C_2H_2$ , or  $30C_2H_2$  be combined with H.

In acetic acid, metacetic acid, butyric acid, valerianic acid, even up to melissic acid, radicals occur =  $C_4H_3, C_6H_5, C_8H_7, C_{10}H_9$ , . . . . .  $C_{60}H_{59}$ . The difference between the individual radicals is the same as in the methyl group, only the carbon exceeds the hydrogen by 1 atom. If, from the first member acetyl  $C_4H_3$  we withdraw  $C_2H_2$  there remains formyl =  $C_2H$ . This latter corresponds to the H in the methyl group; hence it is the active molecule in the whole series; the individual members appear hence as a combination of  $C_2H$  with  $C_2H_2, 2C_2H_2, 3C_2H_2$  . . . . .; they all combine, like formyl, with  $O_3$  to form acids, and also give, so far as experiments have been made, equivalent compounds with the remaining negative elements. From what has been said, it is evident that each member of the methyl group must correspond to one of the formyl. Thus H in the methyl series equals  $C_2H$  in the formyl series, and in the same manner is

Methyl	$C_2H_2, H$	like	Acetyl	$C_2H_2, C_2H$
Ethyl	$2C_2H_2, H$	“	Metacetyl	$2C_2H_2, C_2H$
Amyl	$5C_2H_2, H$	“	Capronyl	$5C_2H_2, C_2H$ , etc.

If the active element H in the methyl group receives  $C_2$ , we obtain thus the corresponding member of the formyl group; thus cyanogen  $NC_2$  brought in contact with methyl  $C_2H_2, H$  gives nitro-acetyl  $2(C_2H_2, C_2H)N$ ; in the same manner, cyanogen and

Conversion of the radicals of the methyl group into those of the formyl, and the reverse.

ethyl  $2C_2H_2, H$  give nitro-metacetyl  $(2C_2H_2, C_2H)N$ . If we let foreign oxygen act upon the radicals of the methyl group, the ascending  $C_2H_2$  is first affected, whilst  $H_2$  oxidizes,  $C_2$  combines with the active  $H$  to form  $C_2H$ . The radical of the formyl group which is thus formed always stands about one member lower than that of the methyl group out of which it arises. Thus goes

Methyl	$C_2H_2, H$	over into	Formyl	$C_2H$ .
Ethyl	$2C_2H_2, H$	"	Acetyl	$C_2H_2, C_2H$ .
Amyl	$5C_2H_2, H$	"	Valeryl	$4C_2H_2, C_2H$ .

By the conversion of oxide of ethyl  $(2C_2H_2, H)O$  into acetic acid,  $(C_2H_2, C_2H)O_3$ , arises first  $(C_2H_2, C_2H)O$ , and then by the oxidation of this compound acetic acid, *but which the moment that it is formed combines with another atom of undecomposed oxide of ethyl*; hence, in the commencement, we obtain  $(2C_2H_2, H)O + (C_2H_2, C_2H)O_3 = C_8H_8O_4 = C_4H_4O_2$ ; afterwards, the second atom of oxide of ethyl goes over first by the presence of oxygen into acetic acid; thus, by the oxidation of the oxide of amyl  $(5C_2H_2, H)O$  we obtain, first, valerianate of amyl  $5(C_2H_2, H)O + (4C_2H_2, C_2H)O_3 = C_{20}H_{20}O_4 = C_{10}H_{10}O_2$ .

Quite analogous to that of oxygen is the behavior of the halogens in their action upon the members of the methyl group; they act, first of all, upon  $C_2H_2$ , set  $C_2$  free by forming 2 atoms hydrochloric acid, this  $C_2$  combines with the active  $H$  to form  $C_2H$ . Hence, by the first action of chlorine upon oxide of ethyl arises oxide of acetyl  $(C_2H_2, C_2H)O$ ; but since the latter, owing to the presence of oxygen, oxidizes, forming acetic acid, by the presence of chlorine there is formed oxychloride of acetyl;  $(C_2H_2, C_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$  that is acetic acid in which  $O_2$  is substituted by  $Cl_2$ . Like acetic acid, also, the oxychloride of acetyl combines the moment it is formed with another atom of undecomposed oxide of ethyl to form  $(2C_2H_2, H)O + (C_2H_2, C_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right. = C_8H_8Cl_2O_2 = C_4H_4ClO$ ; by the farther action of chlorine the second atom of oxide of ethyl goes over also into oxychloride of acetyl; if we treat this compound with potassa, we obtain chloride of potassium and acetate of potassa. If upon chlor-ethyl  $(2C_2H_2, H)Cl$  we let chlorine act, there is thus formed first a compound of chlor-ethyl with chloride of acetyl  $(C_2H_2, C_2H)Cl_3$ , and then pure chloride of acetyl. If we treat this compound with an alcoholic solution of potassa, we obtain chloride of potassium and acetate of potassa.

*It may be generally stated that by the conversion of the radicals*

of the methyl group into those of the formyl group, always in the commencement combinations of both arise. The same is true of the radicals of the other classes.

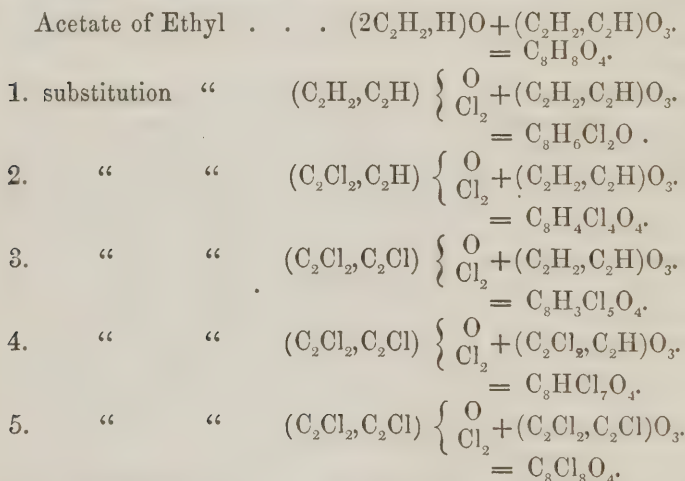
Conversion of the primary radicals into the derived.

From what has been said of the conversion of the radicals of the methyl group into those of the formyl group, it is self-evident that to those of the former no derived radicals correspond; that is, no substitution of hydrogen by the halogens can take place, since they at once go over into the corresponding members of the formyl group. We can certainly, for example, consider the compound  $C_8Cl_8O_4$  which arises by the action of chlorine upon acetate of ethyl, as constituted of  $(C_4Cl_5)O + (C_4Cl_3)O_3$ ; from the behavior to potassa, however, it would appear that it consists of  $(C_4Cl_3) \left\{ \begin{array}{l} O \\ Cl_2 \end{array} + (C_4Cl_3)O_3 \right.$ ; thus may the substances which arise by the first action of chlorine upon chlor-ethyl, and are constituted of  $(C_4H_5)Cl + (C_4H_3)Cl_3$  be viewed as chlor-ethyl in which 1 at. of chlorine is substituted by 1 at. hydrogen, but then must also the acetate of ethyl show oxide of ethyl in which 1 at. hydrogen is replaced by 1 at. oxygen; the erroneousess of this opinion is made evident from the decomposition of the substance by pure potassa.

On the other hand, if the halogens act upon the radicals of the formyl group, substitution takes place in such a way that the ascending molecules  $C_2H_2, 2C_2H_2, 3C_2H_2 \dots$  gradually go over into  $C_2Cl_2, 2C_2Cl_2, 3C_2Cl_2 \dots$  or into  $C_2Br_2, 2C_2Br_2, \dots$  and take the place of the first in the radicals. In most cases, then, the active molecule  $C_2H$  in the radicals is first by the action of chlorine led over into  $C_2Cl$ , when all passive molecules  $C_2H_2$  are converted into  $C_2Cl_2$ . The original character of the primary radical is changed by these substitutions only so far, that (as has been already remarked) in proportion as the halogens enter, the radical receives a negative character. All the atoms of the halogens, which substitute hydrogen in the radicals, oppose the action of potassa because oxygen never enters as a constituent of a radical. By the decomposition of acetic acid  $HIO(C_2H_2, C_2H)O_3$  by chlorine, arises first bichlor-acetic acid  $HIO(C_2Cl_2, C_2H)O_3$  which the moment it arises, forms with one atom of acetic acid a double acid  $= HO(C_2H_2, C_2H)O_3 + HIO(C_2Cl_2, C_2H)O_3$ , which may be also considered as acetic acid in which one atom of hydrogen was substituted by one atom of chlorine; but this compound corresponds to the acetate of ethyl, or acetyl-chlorate of chlor-ethyl. By continued action of chlorine the second atom of acetic acid goes over into bichlor-acetic acid, and this finally into chlor-acetic acid  $HIO(C_4Cl_3)O_3$ . In like manner, chloride of acetyl  $(C_2H_2, C_2H)Cl_3$ , changes first into chloride of bichlor-acetyl  $(C_2Cl_2, C_2H)Cl_3$ , and finally into chloride of ter-chlor-acetyl  $(C_2Cl_2, C_2Cl)Cl_3 = (C_4Cl_3)Cl_3$ ,



and only the chlorine atoms which are combined with the radical  $C_4Cl_3$  can be substituted by oxygen atoms. Butyric acid  $HO(3C_2H_2C_2H)O_3$ , brought in contact with chlorine, forms first bichlor-butyric acid  $HO(C_2Cl_2, 2C_2H_2, C_2H)O_3$ , and then tetrachlor-butyric acid  $HO(2C_2Cl_2, C_2H_2, C_2H)O_3$ . In the same manner valerianic acid  $HO(4C_2H_2, C_2H)O_3$ , is converted at first into bichlor-valerianic acid,  $HO(C_2Cl_2, 3C_2H_2, C_2H)O_3$ , and then into tetrachlor-valerianic acid  $HO(2C_2Cl_2, 2C_2H_2, C_2H)O_3$ ; in complete substitution  $HO(4C_2Cl_2, C_2Cl)O_3$  must be formed. If upon formate of methyl  $(C_2H_2, H)O + (C_2H)O_3$ , we let chlorine act, we obtain after a little  $(C_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} + (C_2H)O_3; (C_2Cl) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} + (C_2H)O_3, \text{ and } (C_2Cl) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} + (C_2Cl)O_3 = C_4Cl_4O_4$ . If we treat the latter compound with wood spirit we obtain chlor-formate of methyl  $(C_2H_3)O + (C_2Cl)O_3 = C_4H_3ClO_4$ ; thus only the two atoms of chlorine withdraw and are replaced by oxygen, which in the compound  $(C_2Cl) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right\}$  do not occur in the radicals. Acetate of ethyl is gradually led over by chlorine into the following combinations:—



By the combining of the first substitution with one atom of undecomposed acetate of ethyl arises  $C_8H_7ClO_4$ , and by that of the second with the third  $C_8H_5Cl_3O_4$ . If we treat the fifth substitution with an alcoholic solution of potassa, we obtain  $(C_2Cl_2, C_2Cl)O_3 = C_8Cl_6O_6$ ; hence only two atoms of chlorine withdraw, and are replaced by oxygen, which is not contained in the radical. As yet but few derived radicals of the formyl group are known in which hydrogen is replaced by  $NO_4$ .

As in the formation of derived radicals the atoms of hydrogen are replaced by an equal number of chlorine atoms, it may be also



that in the derived, chlorine is substituted by hydrogen, whereby these are again reconverted into primary. This case occurs, for instance, when potassium or another positive metal and hydrogen work simultaneously upon a derived radical. In the same moment that the positive metal unites with the halogens an equal number of atoms of hydrogen enter in their place. Here comes into view: 1st, the great affinity of chlorine for the metals, and 2d, the inclination of the carbon atoms to form with hydrogen positive radicals which show great opposition to the negative oxygen. Thus chlor-acetic acid  $\text{HO}(\text{C}_2\text{Cl}_2, \text{C}_2\text{Cl})\text{O}_3$ , with six atoms potassium amalgamated with mercury, and three atoms water simultaneously brought in contact gives again acetic acid  $\text{HO}(\text{C}_2\text{H}_2, \text{C}_2\text{H})\text{O}_3$ ; if we use less potassium we obtain the middle member  $\text{HO}(\text{C}_2\text{H}_2, \text{C}_2\text{Cl})\text{O}_3$ . Chloride of chlor-formyl  $(\text{C}_2\text{Cl})\text{Cl}_3$  by the same treatment is converted into chlor-methyl  $(\text{C}_2\text{H}_3)\text{Cl}$ , and hereupon into hydro-methyl. (Marsh gas)  $(\text{C}_2\text{H}_3)\text{H}$ , in this manner by the action of chlorine upon hydro-methyl arises in the commencement  $(\text{C}_2\text{H})\text{Cl}_3$ , and then  $(\text{C}_2\text{Cl})\text{Cl}_3$ . These transpositions are fully explained by the chemical character of the new radicals, which has been fully developed above.

As in the primary so also in the entirely or partially derived radicals, must the individual components be thought united as in a whole, for only in their totality do they produce molecules which assume the place of elements in the compounds; the derived radicals also give two vol. gas. First, by the union of these primary or derived radicals with each other, or with inorganic matter, the real paired radicals, as well as the double radicals are obtained, whose gaseous atomic volume is mostly four vol., or like that of the single radicals.

*Chlor-methyl gas*  $(\text{C}_2\text{H}_2, \text{H})\text{Cl}$  led through a glowing porcelain tube, separates into methylen  $\text{C}_2\text{H}_2$ , and into  $\text{HCl}$ ; in the same manner from chlor-ethyl  $(2\text{C}_2\text{H}_2, \text{H})\text{Cl}$ ; we obtain elayl  $\text{C}_4\text{H}_4$  and  $\text{HCl}$ . The formation of these bodies can be simply explained by the assumption that the active H in methyl or ethyl joins to the chlorine, and thereby the components  $\text{C}_2\text{H}_2, 2\text{C}_2\text{H}_2$  are set free as independent radicals. But, with this explanation, the other relations of these bodies do not agree; thus these radicals do not correspond to two, but to four vol. of gas. According to this opinion elayl  $2\text{C}_2\text{H}_2$ , by loss of one atom of hydrogen, must be converted into acetyl  $(\text{C}_2\text{H}_2, \text{C}_2\text{H})$ ; but this is not the case, as is apparent from the phenomena of the substitution of elayl. All the phenomena which methylen and especially elayl present are explained consequently when these are considered as paired double radicals arising from those of the methyl group with those of the formyl. According to this opinion elayl appears as a compound of methyl with formyl  $= (\text{C}_2\text{H}_3)^-(\text{C}_2\text{H})$

Conversion of the derived radicals into the primary.

Paired radicals formed by the union of the radicals of the methyl group with those of the formyl.

Elayl group.

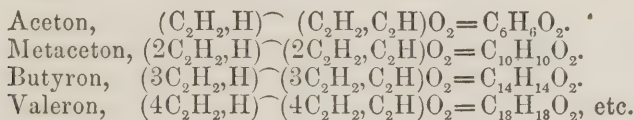
$=\text{Me}, \text{Fo} = 2$  vol. methyl gas + 2 vol. formyl gas = 4 vol. elayl gas. By the formation of elayl from chlor-ethyl, chlorine does not go to the active H, but to one atom hydrogen of  $\text{C}_2\text{H}_2$  and forms  $\text{C}_2\text{H}$  or formyl, whilst the yet remaining elements unite to form methyl  $(\text{C}_2\text{H}_2, \text{C}_2\text{H}_2\text{H})\text{Cl} - \text{HCl} = \text{C}_2\text{H}_3, \text{C}_2\text{H}$ . Whilst, therefore, in ethyl, all atoms are united to form a common organic molecule, elayl appears as a double radical consisting of methyl and formyl, both as independent radicals; according to this view, methylen  $\text{C}_2\text{H}_2$  appears as a combination of hydrogen with formyl  $=\text{H}, \text{Fo}$  in which H corresponds to methyl in elayl. Thus metelayl  $\text{C}_6\text{H}_6$  is constituted of ethyl  $\text{C}_4\text{H}_5$ , and formyl  $=(\text{C}_4\text{H}_5)(\text{C}_2\text{H})$ . By combination of formyl with the ascending members of the methyl group arises therefore a row of double radicals, all of which correspond to four vol. in the gaseous form; and of these, each successive member contains  $\text{C}_2\text{H}_2$  more than the corresponding. Thus is—

*Methylen*:  $\text{H}, \text{Fo} = \text{C}_2\text{H}$ ; *Elayl*:  $\text{Me}, \text{Fo} = \text{C}_4\text{H}_4$ ; *Metelayl*:  
 $\text{Ae}, \text{Fo} = \text{C}_6\text{H}_6$ , &c.

The radicals of this group which we call the elayl group all possess the property to unite themselves directly with two atoms of the halogens. Chlor-elayl is, therefore, a paired compound of chlor-methyl with chlor-formyl  $=\text{MeCl} \text{FoCl}$ . If we treat chlor-elayl with an alcoholic solution of potassa, we obtain a paired compound of  $\text{C}_2\text{H}_2, \text{H}$  with chlor-formyl  $=\text{C}_2\text{H}_2, \text{H} + \text{FoCl}$ , attended with the formation of chloride of potassium and water. This body (the paired compound) is directly combined with two atoms of chlorine and forms a paired compound of  $(\text{C}_2\text{H}_2, \text{Cl} + \text{HCl}) \text{FoCl}$ . This substance has the same elementary constitution as chloride of acetyl  $(\text{C}_2\text{H}_2, \text{C}_2\text{H})\text{Cl}_3$ ; but the latter gives with an alcoholic solution of potassa chloride of potassium and acetic acid; on the contrary the compounds arising from elayl separate into two atoms  $\text{FoCl}$ , forming chloride of potassium and water. If upon chlor-elayl  $(\text{C}_2\text{H}_2, \text{H})\text{Cl} (\text{C}_2\text{H})\text{Cl}$ , we let chlorine act, we first obtain  $(\text{C}_2\text{H})\text{Cl}_3 (\text{C}_2\text{H})\text{Cl} = \text{C}_4\text{H}_2\text{Cl}_4$ , then  $(\text{C}_2\text{Cl})\text{Cl}_3 (\text{C}_2\text{H})\text{Cl} = \text{C}_4\text{HCl}_5$ , and finally  $(\text{C}_2\text{Cl})\text{Cl}_3 (\text{C}_2\text{Cl})\text{Cl} = \text{C}_4\text{Cl}_6$ . If the last compound were identical with chloride of chlor-acetyl  $(\text{C}_4\text{Cl}_3)\text{Cl}_3$ ; a transposition would follow the last action of chlorine.

Hydrate of acetic acid, led as vapor over heated hydrate of potassa, separates into hydro-methyl (marsh gas) Acetonyl group.  $(\text{C}_2\text{H}_3)\text{H}$ , and into two atoms of carbonic acetic acid  $\text{HO}(\text{C}_2\text{H}_2, \text{C}_2\text{H})\text{O}_3 = (\text{C}_2\text{H}_2, \text{H})\text{H} + 2\text{CO}_2$ . There is, therefore, combined with four atoms of oxygen  $\text{C}_2$  from the active  $\text{C}_2\text{H}$ ; thereby methyl arises, which remains combined with the hydrogen of the hydrate water. If we subject the hydrate of acetic acid to the influence of heat without the action of potassa, or of neutral anhydrous acetic salts, we obtain acetone  $\text{C}_6\text{H}_6\text{O}_2$ .

and  $2\text{CO}_2$ . In this case two atoms of acetic acid take part in the decomposition; since four atoms of oxygen combine with two atoms of carbon in the active  $\text{C}_2\text{H}$  from one atom of acetic acid, methyl  $\text{C}_2\text{H}_3$  is formed; at the same time the second atom of acetic acid, by the loss of O, is converted into acetous acid  $(\text{C}_4\text{H}_3)\text{O}_2$ , with which methyl combines as a pairling. Hence the formula for acetone is  $\text{C}_2\text{H}_3\text{-(C}_4\text{H}_3)\text{O}_2=\text{Me, ^AcO}_2$ =four vol. gas, or, also,  $\text{MeO, ^AcO}$ , in which case it appears as a paired compound of oxide of methyl with oxide of acetyl. All the decompositions of acetone agree with the opinion that it contains methyl and acetyl. Its elayl  $\text{Me, ^Fo}$ , then is the radical of acetone  $\text{Me, ^Ac}$ . As acetone from acetic acid, so arises butyrene  $\text{C}_{14}\text{H}_{14}\text{O}_2$  from butyric acid  $\text{C}_8\text{H}_7\text{O}_3$ . Hence the formula for butyrene is  $\text{C}_6\text{H}_7\text{-(C}_8\text{H}_7)\text{O}_2$ ; all radicals of the group which we call the acetonyl group, are combinations of the methyl group with the corresponding members of the formyl group. Therefore these radicals also form an ascending series in which, however, the difference between the individual members is not  $\text{C}_2\text{H}_2$ , but  $2\text{C}_2\text{H}_2=\text{C}_4\text{H}_4$ .



If we treat acetone, in the cold, with hydrated sulphuric acid, it separates into water and oxide of mesityl  $\text{C}_6\text{H}_5\text{O}$ ; oxide of metacetonyl has also the same elementary constitution, but it consists of  $(2\text{C}_2\text{H}_2, \text{C}_2\text{H})\text{O}$ ; the former, on the contrary, is a paired compound  $=\text{C}_2\text{H}_2\text{-(C}_4\text{H}_3)\text{O}$ , corresponding to the chlorine compound in the elayl group:  $\text{C}_2\text{H}_2\text{-(C}_2\text{H})\text{Cl}$ .

By the dry distillation of glycerine  $\text{C}_6\text{H}_7\text{O}_5$ , it separates into three atoms,  $\text{HO}$ , and into oxyhydrate of acryl  $\text{HO, (C}_6\text{H}_3)\text{O}=\text{C}_6\text{H}_4\text{O}_2$ ; by oxidation this compound goes over into acrylic acid  $\text{HO, (C}_6\text{H}_3)\text{O}_3$ . If we bring <sup>Acryl.</sup> a strong alkaline solution of this acid in contact with the air, it separates by absorption of oxygen into formic acid and acetic acid; hence it follows that acryl  $\text{C}_6\text{H}_3$  must be a paired radical. If we suppose the pairling to be  $\text{C}_4\text{H}_2$ , then this pairling with formic acid  $(\text{C}_2\text{H})\text{O}_3$  is acrylic acid; the formula hence is  $\text{C}_4\text{H}_2\text{^FoO}_3$ . In decomposition the pairling leaves formic acid, and with 2 at. oxygen and the elements of 1 at. water it forms acetic acid:  $\text{C}_2\text{H}_2+\text{O}_2+\text{HO}=(\text{C}_4\text{H}_3)\text{O}_3$ . As acrylic acid appears as a paired formic acid, so the primary acids of chlor-succinic acid appear as paired acetic acid:  $\text{C}_2\text{H}_2\text{, ^AcO}_3$ , and lactic acid as a paired compound  $=\text{C}_2\text{H}_2\text{-(C}_4\text{H}_3)\text{O}_5=\text{C}_4\text{H}_4\text{O}_2\text{, ^FoO}_3$ .

## SECOND CLASS.

## HYDROPOLYCARBYLS.

*First Group.*

Oleyl group. Component,  $C_2H_2$ ; Nucleus,  $C_2$ ; Active Part,  $C_2H=C_6H_3$ .

If between the components and the active part of the formyl group the nucleus  $C_2$  enters, we obtain radicals which combine with 3 atoms of oxygen to form acids; the higher members are ranked directly with the higher members of the formyl group; the best known of these acids is oleic acid. The constitution of the radicals of this group is,

Member 1.	Terecyl,	$C_2H_2, C_2, C_2H=C_6H_3$ .
"	2. Unknown,	$2C_2H_2, C_2, C_2H=C_8H_5$ .
"	3. Camphyl,	$3C_2H_2, C_2, C_2H=C_{10}H_7$ .
"	13. Moringyl,	$13C_2H_2, C_2, C_2H=C_{30}H_{27}$ .
"	16. Oleyl,	$16C_2H_2, C_2, C_2H=C_{36}H_{33}$ .
"	17. Doeglyl,	$17C_2H_2, C_2, C_2H=C_{38}H_{35}$ .
"	20. Erucyl,	$20C_2H_2, C_2, C_2H=C_{44}H_{41}$ .

All radicals contain three atoms more of carbon than of hydrogen.

Succinic acid, lipinic, adipinic, pirnelinic, suberic, and sebacic acid, form an eminently distinguished class of acids. According to the most accurate investigation, succinic acid, in all its relations, particularly in the succin-sulphuric acid, and in the phenomena of substitution by chlorine, may be considered with certainty as a double acid; that is, as consisting of two acids, each of which retains in the compound its own absorbing capacity. If upon acetic acid anhydrous sulphuric acid be left to act, we thus obtain a paired double acid =  $2HO(C_2H_2, C_2SO_2)O_3, \sim SO_3$ , as a compound of sulphuric acid with acetic, in which the active H in  $C_2H$  is substituted by  $SO_2$ ; this acid saturates 2 at. base. Quite in the same way, the above-mentioned acids may be considered as double acids, consisting of formic acid, with the different acids of the oleyl group: these acids all saturate 2 at. base. Their formation speaks in favor of this opinion: if, for instance, they arise by the oxidation of oleic acid, and the higher members of the acids of the formyl group; sebacic acid, however, can only be obtained by the dry distillation of oleic acid.



According to this assumption, the constitution of these acids is:

Succinic acid,	$2\text{HO}(\text{C}_6\text{H}_3)\text{O}_3, \text{FoO}_3 = \text{C}_8\text{H}_4\text{O}_6.$
Lipinic	$" \quad 2\text{HO}(\text{C}_8\text{H}_5)\text{O}_3, \text{FoO}_3 = \text{C}_{10}\text{H}_6\text{O}_6.$
Adipinic	$" \quad 2\text{HO}(\text{C}_{10}\text{H}_7)\text{O}_3, \text{FoO}_3 = \text{C}_{12}\text{H}_8\text{O}_6.$
Pimelinic	$" \quad 2\text{HO}(\text{C}_{12}\text{H}_9)\text{O}_3, \text{FoO}_3 = \text{C}_{14}\text{H}_{10}\text{O}_6.$
Suberic	$" \quad 2\text{HO}(\text{C}_{14}\text{H}_{11})\text{O}_3, \text{FoO}_3 = \text{C}_{16}\text{H}_{12}\text{O}_6.$
Sebacic	$" \quad 2\text{HO}(\text{C}_{18}\text{H}_{15})\text{O}_3, \text{FoO}_3 = \text{C}_{20}\text{H}_{16}\text{O}_6.$

By the action of chlorine upon succinate of ethyl  $2(\text{C}_4\text{H}_5)\text{O} + (\text{C}_6\text{H}_3)\text{O}_3, \text{FoO}_3$ , we finally obtain a compound which consists of  $\text{C}_{16}\text{HCl}_{13}\text{O}_8 = [2(\text{C}_2\text{Cl}_2, \text{C}_2\text{Cl} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right\}) (\text{C}_6\text{Cl}_3)\text{O}_3, \text{FoO}_3]$ . If we heat this compound to  $290^\circ$ , a smoking fluid goes over (with evolution of carbonic acid), which, brought in contact with water, separates into hydrochloric acid, chlor-acetic acid, and into chlor-succinic acid  $\text{C}_6\text{Cl}_3\text{H}_2\text{O}_3$ . Hydrochloric acid and chlor-acetic acid  $(\text{C}_2\text{Cl}_2, \text{C}_2\text{Cl})\text{O}_3$ , arise by the decomposition of oxychloride of chlor-acetyl;  $(\text{C}_2\text{Cl}_2, \text{C}_2\text{Cl}) \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix} \right.$ . If the nucleus leave  $(\text{C}_6\text{Cl}_3)\text{O}_3 = (\text{C}_2\text{Cl}_2, \text{C}_2, \text{Cl})$  we obtain chlor-acetyl;  $\text{C}_4\text{Cl}_3$ . Now, chlor-succinic acid is  $(\text{C}_6\text{Cl}_3)\text{O}_3, \text{FoO}_3 + \text{HO} = \text{C}_6\text{Cl}_3\text{H}_2\text{O}_3 = \text{C}_2\text{H}_2(\text{C}_4\text{Cl}_3)\text{O}_3 + 2\text{CO}_2$ . If we treat the compound arising from the action of chlorine upon succinate of ethyl, with alcohol, we obtain, upon addition of water, hydrochloric acid, carbonate, chlor-acetate, and chlor-succinate of ethyl; if we shake the same with ammonia, thus arise chloride of ammonium, chlor-acetamid  $\text{NH}_2(\text{C}_4\text{Cl}_3)\text{O}_2$ , and chlor-succinate of ammonia. These decompositions are explained in a simple manner by the received formula for succinic acid.

### Second Group.

The second group of the radicals of the hydro polycarbyls includes:—

- The Nicyl group; Component  $\text{C}_9\text{H}_2$ ; Nucleus  $\text{C}_6$ ; Active part  $\text{H} = \text{C}_8\text{H}_3$ .
- The Niceyl group; Component  $\text{C}_2\text{H}_2$ ; Nucleus  $\text{C}_6$ ; Active part  $\text{C}_2\text{H} = \text{C}_{10}\text{H}_3$ .

The niceyl group behaves to the nicyl group as the formyl to the methyl. If we lead chlorine gas into a solution of 1 part benzoic acid  $(2\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3 = \text{C}_{14}\text{H}_5\text{O}_3$ , and 3 to 4 parts hydrate of potassa in 5 parts water, we thus obtain chlor-niceinic acid  $= \text{C}_{12}\text{H}_4\text{ClO}_3$ , attended with evolution of carbonic acid. Without doubt, niceinic acid  $(2\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3 = (\text{C}_{12}\text{H}_5)\text{O}_3$  is formed, and only by the continued action of chlorine a compound of niceinic acid with bichlor-niceinic acid  $\text{HO} =$

$(\text{C}_{12}\text{H}_5)\text{O}_3 + \text{HO}(\text{C}_2\text{Cl}_2\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3 = (\text{C}_{12}\text{H}_4\text{Cl})\text{O}_3$ . Were pure hydrate of niceinic acid known isolated, it would separate by dry distillation with hydrate of lime into hydro-nicyl  $(2\text{C}_2\text{H}_2, \text{C}_6, \text{H})\text{H}$ , and carbonic acid, as hydrate of acetic acid into hydro-methyl and



carbonic acid; this compound then would behave to niceinic acid as hydro-methyl to acetic acid:—

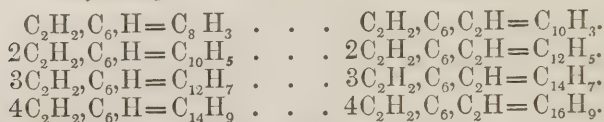
Hydro-nicyl ( $2C_2H_2, C_6, H$ )H = niceinic acid ( $2C_2H_2, C_6, C_2H$ )O<sub>3</sub>.

Hydro-methyl ( $C_2H_2H$ )H = acetic acid ( $C_2H_2, C_2H$ )O<sub>3</sub>.

If between the active and the passive part of the methyl group the nucleus  $C_6$  enters, we obtain the corresponding members of the nicyl group, and similarly the formyl group is converted into the niceyl group. The formulæ for the radicals of these groups are hence:—

Nicyl Group.

Niceyl Group.



As yet only the second members in combination with chlorine are known; Chlornicyl (Chlornicid) ( $C_{10}H_5$ )Cl is obtained by the dry distillation of chlorniceinic acid with an excess of hydrate of lime.

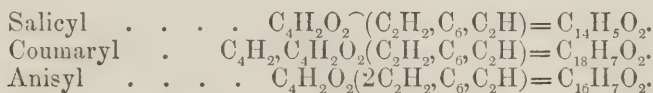
#### PAIRED RADICALS OF THESE GROUPS.

**Furfural.** By the distillation of flour or wheat bran with sulphuric acid, we obtain an oily compound—furfural, which consists of  $C_{10}H_4O_4$ . It corresponds in its gaseous state to 4 volumes, whence it appears that it contains no simple radical. Of the 4 atoms of oxygen, 2 atoms may be replaced by sulphur; hence I consider furfural as a paired compound consisting of  $C_2HO_2$  as a pairling combined with the first member of the nicyl group =  $C_2HO_2 \wedge (C_2H_2, C_6, H)O_2$ ; the sulphur compound then consists of  $C_2HO_2 \wedge (C_2H_2, C_6, H)S_2$ .

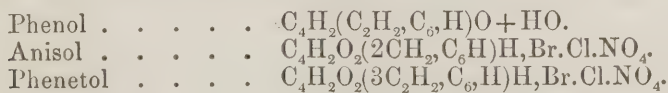
**Salicyl.** If a strong alkaline solution of salicylous acid  $HO, C_{14}H_5O_3$  be brought in contact with the air, it separates (as acric acid into acetic and formic acid) into acetic acid and melanic acid  $C_{10}H_4O_5$ ; by oxidation we obtain salicylic acid =  $HO, C_{14}H_5O_5$ , which, in chemical relations, behaves itself quite like benzoic acid  $HO, C_{14}H_5O_3$ . The separation of salicylous acid into acetic and melanic acid indicates a paired radical. If we subtract as a pairling  $C_4H_2O_2$  (the pairling of lactic acid), there remains for salicylous acid ( $C_{10}H_3$ )O, and for salicylic acid ( $C_{10}H_3$ )O<sub>3</sub> = ( $C_2H_2, C_6, C_2H$ )O and ( $C_2H_2, C_6, C_2H$ )O<sub>3</sub>. The formulæ for the acids are hence:  $HO, C_4H_2O_2 \wedge (C_2H_2, C_6, C_2H)O$  and  $HO, C_4H_2O_2 \wedge (C_2H_2, C_6, C_2H)O_3$ . If the pairling  $C_4H_2O_2$  separates, it forms with the elements of one atom HIO acetic acid. *Cou-*

*marylous acid* holds the same relations to *coumarylic acid* that salicylous acid holds to salicylic acid. Both compounds, by treatment with hydrate of potassa, go over into salicylic acid under evolution of hydro-carbon. Now, coumaryl-

lous acid consists of  $\text{HO}, \text{C}_{18}\text{H}_7\text{O}_3$ , and coumarylic acid of  $\text{HO}, \text{C}_{18}\text{H}_7\text{O}_5$ . If from both we withdraw salicylous and salicylic acid, there remains  $\text{C}_4\text{H}_2$ . Hence, coumarylous acid consists of  $2\text{C}_4\text{H}_2 + \text{O}_2 \wedge (\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}$ , and coumarylic acid of  $2\text{C}_4\text{H}_2 + \text{O}_2 \wedge (\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3$ , or there are compounds of salicylous acid and salicylic acid with the pairing  $\text{C}_4\text{H}_2$ . Farther, to this group belong anisylous acid  $\text{HO}, \text{C}_{16}\text{H}_7\text{O}_3$  and anisyllic acid  $\text{HO}, \text{C}_{16}\text{H}_7\text{O}_5$ . The difference between these and the compounds of salicyl is  $\text{C}_2\text{H}_2$ ; therefore, anisylous acid consists of  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \wedge (2\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}$  and anisyllic acid of  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \wedge (2\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3$ . The formulæ for the paired radicals of these compounds are hence:—



If we subject salicylic acid to dry distillation, we thus obtain, under formation of carbonic acid, phenol  $\text{C}_{12}\text{H}_6\text{O}_2$ . Phenol. Phenol is a hydrate, for it forms with potassa a compound  $\text{KO}, \text{C}_{12}\text{H}_5\text{O}$ , resembling ether-potassa  $\text{KO}, \text{C}_4\text{H}_5\text{O}_5$ . In the same manner it gives, with sulphuric acid, one of the paired acids  $= \text{HO}(\text{C}_{12}\text{H}_5\text{O}, \text{SO}_3) \wedge \text{SO}_3$ , corresponding to ether-sulphuric acid. Therefore, in the formation of spiol, 2 at. oxygen leave the pairing, and 2 at. oxygen leave the acid; out of  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \wedge (\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3$  is withdrawn  $\text{HO}, \text{C}_4\text{H}_2 \wedge (\text{C}_2\text{H}_2, \text{C}_6, \text{H})\text{O} = \text{HO}, \text{C}_{12}\text{H}_5\text{O}$ . If salicylate of methyl with baryta be subjected to dry distillation, we obtain anisol  $\text{C}_{14}\text{H}_8\text{O}_2$ , and in like manner from the salicylate of ethyl is formed phenetol  $\text{C}_{16}\text{H}_{10}\text{O}_2$ . Anisol. Phenetol. Anisol and phenetol contain no hydrate water, and give no compounds with potassa. From their behavior to chlorine and nitric acid, it seems that 1 at. hydrogen not in the radical, is found which may be substituted by chlorine, bromine, and  $\text{NO}_4$ ; hence the formula for anisol is  $= \text{C}_4\text{H}_2\text{O}_2 \wedge (2\text{C}_2\text{H}_2, \text{C}_6, \text{H})\text{H}$ , and that for phenetol  $= \text{C}_4\text{H}_2\text{O}_2 \wedge (3\text{C}_2\text{H}_2, \text{C}_6, \text{H})\text{H}$ .



If we treat phenol with chlorate of potassa and hydrochloric acid, it is converted into chloranil  $\text{C}_{12}\text{Cl}_4\text{O}_4$ : we also obtain the same compound from chinon  $\text{C}_{12}\text{H}_4\text{O}_4$ , by distilling the latter compound with chloride of lime, simultaneously with compounds which correspond to the formulæ  $\text{C}_{12}\text{H}_3\text{ClO}_4$ ,  $\text{C}_{12}\text{H}_2\text{Cl}_2\text{O}_4$ , and  $\text{C}_{12}\text{HCl}_3\text{O}_4$ . Chloranil is hence the derived compound of chinon. If we assume that, in the formation of chloranil from phenol, the nucleus  $\text{C}_6$  is not affected, then is given as formula for chloranil  $\text{C}_2\text{ClO}_2 \wedge (\text{C}_2\text{Cl}_2, \text{C}_6, \text{C}_2\text{Cl})\text{O}_2$ ; Chinon and chloranil.

and, therefore, that of chinon =  $C_2H_2O_2 \wedge (C_2H_2, C_6, C_2H)O_2$ . Chinon behaves to furfural as acetyl to methyl; all compounds of phenol give by the same treatment chloranil. To the paired compounds

of this group belongs also saligenin  $C_{14}H_8O_4$ . By Saligenin.

the action of oxidizing bodies, this latter compound is converted, by formation of water, into the hydrate of salicylous acid. This analysis is simply explained if we assume for the formula of saligenin  $HO, C_4H_4O_2 \wedge (C_2H_2, C_6, C_2H)O$ ; if the pairling

$H_2$  withdraws, salicylous acid remains. In the same Indigo.

manner we may consider indigo-blue as a paired compound of cyanogen with salicyl =  $C_4H_2O_2(C_2H_2, C_6, C_2H) \wedge NC_2 = NC_{16}H_5O_2$ . Therefore is,

Furfural . . . . .	$C_2H_2O_2 \wedge (C_2H_2, C_6, C_2H)O_2$ .
Chinon . . . . .	$C_2H_2O_2 \wedge (C_2H_2, C_6, C_2H)O$ .
Phenol . . . . .	$C_4H_2 \wedge (C_2H_2, C_6, C_2H)O + HO$ .
Creosote (taurylic acid) . . . . .	$C_4H_2 \wedge (2C_2H_2, C_6, C_2H)O + HO$ .
Anisol . . . . .	$C_4H_2O_2 \wedge (2C_2H_2, C_6, C_2H)H$ .
Phenetol . . . . .	$C_4H_2O_2 \wedge (3C_2H_2, C_6, C_2H)H$ .
Salicylous acid . . . . .	$C_4H_2O_2 \wedge (C_2H_2, C_6, C_2H)O + HO$ .
Salicylic acid . . . . .	$C_4H_2O_2 \wedge (C_2H_2, C_6, C_2H)O_3 + HO$ .
Anisylous acid . . . . .	$C_4H_2O_2 \wedge (2C_2H_2, C_6, C_2H)O + HO$ .
Anisyllic acid . . . . .	$C_4H_2O_2 \wedge (2C_2H_2, C_6, C_2H)O_3 + HO$ .

By the action of chlorine upon phenol we obtain three com-

Derived radi-  
cals of this  
group.

pounds which correspond to the formulæ  $HO, C_{12}H_3Cl_2O$ ;  $HOC_{12}H_2Cl_3O$ , and  $HO, C_{12}Cl_5O$ , all of which possess the properties of an acid. Phenol may be

viewed as wood spirit with the nucleus  $C_6$  and the pairling  $C_4H_2$ . In similar manner, as oxide of methyl is converted

by the action of chlorine into oxychloride of formyl  $(C_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$

phenol must form a compound =  $HO, C_4H_2(C_6, C_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$ ; by the

continued action of chlorine must arise  $HO, C_4H_2 \wedge (C_6, C_2Cl) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$

=  $HO, C_{12}H_2Cl_3O$ , and finally  $HO, C_4Cl_2 \wedge (C_6, C_2Cl) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$  =  $HO, C_{12}$

$Cl_5O$ . Hence these compounds behave to phenol as the combina-

tions of formyl and chlorformyl to oxide of methyl or to wood spirit. The compounds which arise by the continued action of

chlorine upon anisol and phenetol belong to the salicyl and anisyl compounds. In the commencement we obtain chlor-anisol:  $C_4H_2$

$O_2 \wedge (2C_2H_2, C_6, C_2H)Cl$  corresponding to chlor-ethyl, by farther action is formed chloride of salicyl  $C_4H_2O_2 \wedge (C_2H_2, C_6, C_2H)Cl$ , correspond-

ing to chloride of acetyl. If chloride of salicyl combines with chlor-anisol, we obtain  $C_4H_2O_2 \wedge (2C_2H_2, C_6, C_2H)Cl + C_4H_2O_2 \wedge (C_2H_2, C_6,$

$C_2H)Cl_3 = C_{14}H_6Cl_2O_2$ . The same relations exist when nitric acid

acts upon the above-mentioned bodies; we obtain the corresponding nitro combinations.

By the action of bromine upon salicylous acid, we first obtain a compound of salicylous acid with bibrom salicylous acid  $= \text{HO}, \text{C}_4\text{H}_2\text{O}_2(\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O} + \text{HO}, \text{C}_4\text{H}_2\text{O}_2(\text{C}_2\text{Br}_2, \text{C}_6, \text{C}_2\text{H})\text{O} = \text{HO}, \text{C}_{14}\text{H}_4\text{BrO}_3$ , and then bibrom salicylous acid, etc.

### Third Group.

Component  $\text{C}_2\text{H}_2$ ; Nucleus,  $\text{C}_8$ ; Active Element,  $\text{H}=\text{C}_{10}\text{H}_3$ .  
 "  $\text{C}_2\text{H}_2$ ; "  $\text{C}_8$ ; Active Part,  $\text{C}_2\text{H}=\text{C}_{12}\text{H}_3$ .

As the methyl group by taking  $\text{C}_6$  is converted into the nicid group, so the benzid group is formed by taking the nucleus  $\text{C}_8$ , and in the same manner from the formyl group arises the benzoyl group. The benzoyl group behaves to the benzid group as the methyl to the formyl. Thus corresponds,

Benzid,	$2\text{C}_2\text{H}_2, \text{C}_8, \text{H}$	to Benzoyl,	$2\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H}$ .
Tolid,	$3\text{C}_2\text{H}_2, \text{C}_8, \text{H}$	" Toluyll,	$3\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H}$ .
Xyloid,	$4\text{C}_2\text{H}_2, \text{C}_8, \text{H}$	" Xyloyl, (?)	$4\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H}$ .
Cumid,	$5\text{C}_2\text{H}_2, \text{C}_8, \text{H}$	" Cumyl,	$5\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H}$ .

If we heat the hydrate of benzoic acid with an excess of lime, hydro-benzid (benzin, benzol) arises in the same way as hydro-methyl from the hydrate of acetic acid; from  $(2\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H})\text{O}_3, \text{HO}$  is  $(2\text{C}_2\text{H}_2, \text{C}_8, \text{H})\text{H}$  and  $2\text{CO}_2$ ; thus we obtain hydro-tolid from toluylic acid, and hydro-cumid from cuminic acid. If from ethyl  $2\text{C}_2\text{H}_2\text{H}$ , we subtract 2 at. hydrogen, the result is acetyl  $\text{C}_2\text{H}_2, \text{C}_2\text{H}$ , and if from toolid  $3\text{C}_2\text{H}_2, \text{C}_8, \text{H}$ , we take two atoms H we obtain benzoyl  $2\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H}$ . If we boil hydro-cumid a long time with dilute nitric acid, we obtain toluylic acid and benzoic acid, and thus the radicals of the benzid group, when they combine with the active H, and  $\text{C}_2$  must be converted into the corresponding members of the benzoyl group. If for the formula of phenol we suppose  $\text{HO}(\text{C}_{12}\text{H}_5)\text{O}$ , and for benzin  $(\text{C}_{12}\text{H}_5)\text{H}$ , the first appears as the oxyhydrate of the latter. If these formulæ were correct, phenol must arise from the oxidation of benzin; but this is not the case. Neither benzin nor any compound of the benzid and benzoyl series gives by being treated with hydrochloric acid and chlorate of potassa chloranil. Benzin behaves to phenol as benzoic acid to salicylic acid.

The secondary radicals of the benzid group are as little known as the radicals of the methyl group correspond to the derived, since the first are at once converted into the corresponding members of the benzoyl group. Hence, if upon benzin we let chlorine act, we obtain by the first action  $(\text{C}_{12}\text{H}_5)\text{Cl} + \text{HCl}$ . By farther action, ter-chloride of benzyl  $(\text{C}_2\text{H}_2, \text{C}_8,$

Conversion of the radicals of the benzoyl group into those of the benzid group, and the reverse.

Derived radicals of this group.



$C_2H)Cl_3$  arises from chlor-benzid, just as chloride of acetyl from chlor-ethyl. Thus hydro-tolid  $(3C_2H_2, C_8, H)$  gives with chlorine, first, chlor-tolid;  $(3C_2H_2, C_8, H)Cl$ , and then chloride of benzoyl;  $(2C_2H_2, C_8, C_2H)Cl_3$ . If we boil hydro-tolid a short time with nitric acid, nitro-tolid  $(3C_2H_2, C_8, H)NO_4$ , arises first, and then by continued action benzoyl-nitrid  $(2C_2H_2, C_8, C_2H)3NO_4$ , and by the union of nitrolid with benzoyl-nitrid we obtain the so-called *binitrotolid*.

In the radicals of the benzoyl group we observe the same phenomena of substitution as in those of the formyl group. Thus, by the action of chlorine upon benzoic acid we obtain bichlor-benzoic acid, corresponding to the bichlor-acetic acid. By the combining of bichlor-benzoic acid with benzoic acid arises a double acid =  $2HO(C_2Cl_2, C_2H_2, C_8, C_2H)O_3 + (C_{14}H_5)O_3 = HO(C_{14}H_4Cl)O_3$ , corresponding to the double acid  $2HO(C_2Cl_2, C_2H)O_3 + (C_4H_3)O_3$  which in the commencement is formed by the action of chlorine upon acetic acid. Nitric acid behaves in the same manner.

#### PAIRED RADICALS OF THIS GROUP.

Bitter almond oil  $C_{14}H_6O_2$  in contact with oxygen goes over into hydrate of benzoic acid. If we consider bitter almond oil as oxyhydrate of benzoyl  $HO(C_{14}H_5)O$ , the conversion consists in a simple oxidation. But the remaining relations of bitter almond oil do not coincide with this opinion. These speak decidedly for the acceptance of a radical  $C_{14}H_6$ , which may be obtained isolated, and is converted by oxidation into oil of bitter almonds. If oil of bitter almonds were the hydrated oxide of benzoyl, then must picramyl  $C_{14}H_6$ , analogous to hydro-benzid, consist of  $(C_{14}H_5)H$ ; a supposition which is supported by no facts. On the contrary, if we consider picramyl as a paired radical, consisting of  $C_2H$ , combined with benzid =  $C_2H \wedge (C_{12}H_5) = C_{14}H_6$ , thus are explained all the relations which bitter almond oil presents in a simple manner. It consists then of  $C_2H \wedge (C_2H_2, C_8, H)O_2$ . If the active hydrogen in benzid is withdrawn, and is replaced by the pairling  $C_2H$ , we thus obtain benzoic acid  $(2C_2H_2, C_8, C_2H)O_3$ . We can also suppose that in oil of bitter almonds benzid is the pairling and  $C_2H$  the active =  $C_{12}H_5 \wedge (C_2H)O_2$ .

*Oxide of Cinnamyl*;  $C_{18}H_8O_2$ , behaves to oil of bitter almonds as coumaryl to salicyl; in contact with a concentrated solution of potassa it is at once converted into oil of bitter almonds. Hence, oxide of cinnamyl may be considered as a paired radical, consisting of the pairling  $C_4H_2$ , and of picramyl =  $C_4H_2, Pcr = C_{18}H_8O_2 = C_4H_2(C_2H \wedge 2C_2H_2, C_8, H)O_2$ , and thus also cinnamic appears as benzoic acid with the pairling  $C_4H_2 = C_{18}H_7O_3$ . If we distil hydrate of benzoic acid with hydrate of lime, we obtain hydro-benzid; out of  $(2C_2H_2, C_8, C_2H)O_3$  is  $(2C_2H_2, C_8, H)H$ , and if we subject hydrate of cinnamic

Cinnamid.



acid to the same operation we obtain cinnamin  $C_{16}H_8$ . If cinnamic acid consists of  $HO, C_4H_2, (C_{14}H_5)O_3$ , then must cinnamin correspond to the formula  $C_4H_2(C_{12}H_5)H$ ; it is then a paired compound of  $C_4H_2$  with benzin.

*Naphtalin*:  $C_{20}H_8$ ; it agrees entirely in its chemical properties with benzin, and all the compounds which it forms, and the decompositions it undergoes, are explained in *Naphtalin*.

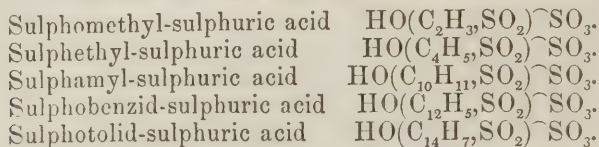
the most simple manner if we consider it as a paired compound, consisting of benzin with the pairing  $C_8H_2$ ; its formula is then  $C_8H_2(C_{12}H_5)H$ . If we let chlorine act upon naphtalin we obtain, in the commencement, a compound  $= C_8H_2(C_{12}H_5)Cl + HCl = C_{20}H_8Cl_2$ ; by the continued action of chlorine then arises  $C_8H_2(C_{12}H_5)Cl_3 + 3HCl = C_{20}H_8Cl_6$ , and by the union of both we obtain  $C_{20}H_8Cl_4$ . If we treat the first compound  $C_8H_2(C_{12}H_5)Cl + HCl$  with potassa, there arises, by formation of chloride of potassium,  $C_8H_2(C_{12}H_5)Cl = C_{20}H_7Cl$ , and if we subject the compound  $C_{20}H_8Cl_6$  to the same operation, we obtain  $C_{20}H_6Cl_2 = C_8H_2(C_{12}H_5)Cl + C_8H_2(C_{12}H_3)Cl_3$ . If upon the compound  $C_8H_2(C_{12}H_5)Cl$  we let chlorine act, we obtain, at first, a compound of  $C_8H_2(C_2H_2, C_3, C_2H)Cl_3$  with  $C_{20}H_7Cl$ , and again  $C_{20}H_6Cl_2$ ; later, the second atom of chlor-naphtalid  $C_{20}H_7Cl$  is converted into  $C_{20}H_5Cl$ , etc. Like the chlorine compounds behave, also, the corresponding nitro-compounds; they appear, therefore, as paired compounds of benzin. In chemical proportions, *Anthracin*  $C_{30}H_{12}$  entirely agrees with naphtalin. With chlorine and nitric acid *Anthracin*. it forms perfectly corresponding compounds; therefore, benzin may be viewed as the active part, and the formula for anthracin may be fixed as  $= C_{18}H_6(C_{12}H_5)H$ . For retisteren, chrysen, pyren, etc., formulæ entirely corresponding are given.

#### *Sulphur Combinations, and Paired Sulphur Acids.*

All radicals which contain II as the active element have the property to combine with  $SO_2$ . The whole class of these bodies has obtained the name of Sulphur compounds. They are obtained by the action of anhydrous sulphuric acid upon the hydrogen compounds of these radicals; their formation, therefore, is consequent upon the union of 1 at. O of  $SO_3$  with H of the above-mentioned radicals. Thus corresponds,

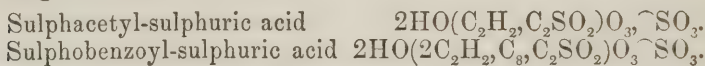
Hydro-methyl	$C_2H_3, II$	to	Sulpho-methyl	$C_2H_3, SO_2$ .
Hydro-ethyl	$C_4H_5, II$	"	Sulpho-ethyl	$C_4H_5, SO_2$ .
Hydro-amyl	$C_{10}H_{11}, H$	"	Sulpho-amyl	$C_{10}H_{11}, SO_2$ .
Hydro-benzid	$C_{12}H_5, H$	"	Sulpho-benzid	$C_{12}H_5, SO_2$ .
Hydro-tolid	$C_{14}H_7, H$	"	Sulpho-tolid	$C_{14}H_7, SO_2$ .
Naphtalin	$2C_4H_2(C_{12}H_5)H$	to	Sulpho-naphtalid	$2C_4H_2(C_{12}H_5), SO_2$ , etc.

These sulphur compounds possess the property as pairings to form with 1 at. hydrated sulphuric acid paired acids, which are called sulpho-sulphuric acids; as—

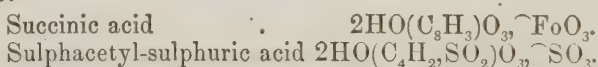


These acids all saturate 1 at. base, and give, with baryta, strontium, lime, and oxide of lead, salts soluble in water. Most of them are very enduring, and their aqueous solution may be boiled without undergoing decomposition.

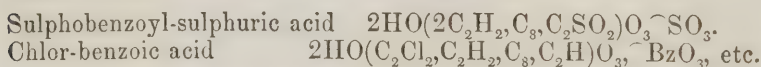
If upon the hydrate of acetic acid we let anhydrous sulphuric acid act, we obtain sulphacetyl-sulphuric acid, and in the same manner hydrate of benzoic acid is converted into sulphobenzoyl-sulphuric acid. The constitution of these acids may be expressed by the following formulæ:—



These acids saturate two atoms base. They exhibit real paired double-acids. Thus, the sulphacetyl-sulphuric acid is to be considered as a compound, consisting of sulphacetic acid; that is, of acetic acid in which H in the active  $\text{C}_2\text{H}$  is substituted by  $\text{SO}_2$ , combined with sulphuric acid; both acids have in their union completely preserved their absorbing capacity; hence they possess the same constitution as the double-acids of the succyl group. Thus is:



Here belong, also, the numerous class of double acids which at first arise by the conversion of the primary into the derived radicals; thus, sulphobenzoyl-sulphuric acid corresponds to chlorbenzoic acid.



Chemical compounds of a higher order can also unite as pairings with acids; as sulphuric acid, phosphoric acid, yes, even carbonic acid, and many organic acids. Thus, the sulphate of ethyl gives with hydrated sulphuric acid ether sulphuric acid =  $\text{HO}(\text{AeO}, \text{SO}_3)\text{SO}_3$ ; in like manner, the carbonate of ethyl combines with carbonic acid to form  $\text{HO}(\text{AeO}, \text{CO}_2)\text{CO}_2$ , and oxalate of ethyl with hydrate of oxalic acid to form  $\text{HO}(\text{AeO}, \text{C}_2\text{O}_3)\text{C}_2\text{O}_3$ . These acids saturate 1 at. base, and give, with alkaline earths and

with oxide of lead, soluble salts; but they are very variable; if we heat their aqueous solutions, they separate into sulphuric acid, etc., and into the corresponding hydrated oxides. Many chemists consider them, hence, not as paired compounds, but as acid salts, similar to the acid sulphates of potassa.

It is very probable that many of the stronger non-volatile organic salts are paired combinations with oxalic acid, and many belong to the class of double acids. Saccharic acid separates at once by heating with concentrated potassa lye into acetic and oxalic acid; the same decomposition is undergone by tartaric acid, malic acid, citric acid, etc. Picramyloxyd-formic acid is a paired compound of bitter almond oil with formic acid.

Non-volatile strong organic acids are probably paired oxalic acids.

*Compounds of Hydrogen and of the Radicals which contain Hydrogen as an active element, with Nitrogen, Phosphorus, Arsenic, and Antimony.*

Nitrogen combines with hydrogen, in many proportions, to form  $\text{NH} = \text{Imid}$ ,  $\text{NH}_2 = \text{Amid}$ ,  $\text{NH}_3 = \text{Ammonia}$ , and  $\text{NH}_4 = \text{Ammonium}$ : but only ammonia  $= \text{NH}_3$  is known isolated. Phosphorus, arsenic, and antimony behave in the same manner. Ammonium behaves like a positive metal to O, S, I, Br, Cl. As was explained above, nitrous acid  $\text{NO}_3$  combines with oxide of ammonium only in consequence of opposite chemical characters. If we heat the compound it separates into water and nitrogen gas,  $\text{NH}_4\text{O} + \text{NO}_3 = 4\text{HO} + 2\text{N}$ . The same decomposition also takes place if the compounds of oxide of ammonium with organic acids, which contain 3 at. oxygen, be subjected to distillation at a higher temperature, or with anhydrous phosphoric acid. If all oxygen atoms from the acid unite to the hydrogen atoms of ammonia, we thus obtain combinations of nitrogen with the radicals of the acids which have obtained the general name of Nitryls. Thus the acetate of ammonium separates into water and nitro-acetyl;  $\text{NH}_4\text{O} + \text{AcO}_3 = 4\text{HO} + \text{AcN}$ . Only oxalates and formate of ammonium, the lowest organic compounds, give cyanogen  $\text{NC}_2$  and hydro-cyanogen  $\text{H}(\text{NC}_2)\text{NH}_4\text{O}$ ,  $\text{C}_2\text{O}_3 = 4\text{HO} + \text{NC}_2$  and  $\text{NH}_4\text{O} + \text{C}_2\text{H}_3\text{O}_3 = 4\text{HO} + \text{H}(\text{NC}_2)$ . In these decompositions, no element occurs with which carbon can unite to form a radical, and present to nitrogen a chemical opposition; this, however, is the case with the higher members of the acids belonging to a group. As acetate of ammonium separates into water and nitro-acetyl, the valerianate of ammonium gives nitro-valeryl, benzoate of ammonium gives nitro-benzoyl. All nitrils behave quite indifferently towards the animal organization, and they all, by the action of strong acids by decomposition of water, are converted into ammonia and the original acids.

Nitrogen compounds.

Formation of nitryls.

The nitrils may also be considered as compounds of cyanogen corresponding to hydro-cyanic acid; thus nitro-acetyl  $(C_4H_3)N$ , may be viewed as cyan-methyl  $(C_2H_3)NC_2$ , and this view is clearly supported by the fact that the same compounds may be obtained by the action of cyanogen upon methyl and ethyl. According to this opinion, cyan-methyl is prussic acid, in which the hydrogen is substituted by methyl; these compounds, however, chemically have not the least resemblance to prussic acid, and they do not act as poisons upon the animal organization. The formation of nitro-acetyl by the action of cyanogen upon methyl is simply explained by the supposition that  $C_2$  of cyanogen unites with the active H of methyl to form acetyl, which remains combined with nitrogen. If in the above-mentioned ammonia salts, or oxide of ammonium compounds, only a partial withdrawing of the hydrogen and oxygen atoms takes place, we obtain either imide or amide; the former correspond to the formula  $NH,RO$ ; the latter are like  $NH_2,RO_2$ . Thus,

Acetamid	consists of	$NH_2, (C_4H_3)O_2$ .
Chloracetamid	"	$NH_2, (C_4Cl_3)O_2$ .
Valeramid	"	$NH_2, (C_{10}H_9)O_2$ .
Benzamid	"	$NH_2, (C_{14}H_5)O_2$ .
Succinamid	"	$2NH_2, (C_8H_4)O_4$ .
Oxamid	"	$NH_2, (C_2)O_2$ , etc.

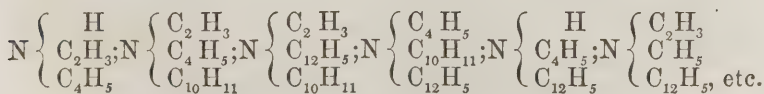
Imide compounds as yet are little known; they, as well as the amid compounds, are indifferent, in part insoluble in water, and by decomposition of water are reconverted into ammonia and the original acids; in their formation rests often the knowledge that one and the same organic radical can form several compounds with oxygen.

Amide as well as imide give, with the acids out of whose salts they were formed, paired acids. As sulfethyl  $C_4H_5,SO_2$  with  $HO,SO_3$  forms sulphethyl-sulphuric, so oxamid  $NH_2,C_2O_2$  combines with oxalic acid  $HIO,C_2O_3$  to form oxamic acid  $=HO(NH_2,C_2O_2)^{\wedge}C_2O_3$ ; thus camphoramid  $NH_2,(C_{10}H_7)O_2$  gives with camphoric acid, camphoramic acid  $=HO(NH_2,C_{10}H_7O_2)^{\wedge}C_{10}H_7O_3$ ; to this class of acids also belong asparaginic acid, sulfamic acid, etc. The camphorate of ammonia  $NH_3,C_{10}H_7O_3$  can itself as pairing (like the sulphate of ethyl) form with 1 atom of hydrate of camphoric acid a paired acid  $=HO(NH_3,C_{10}H_7O_3)^{\wedge}C_{10}H_7O_3$ . These acids saturate 1 at. base, and by decomposition of water are converted into ammonia and the corresponding acids. If upon nitrobenzoic acid, which is a double acid consisting of benzoic and binitrobenzoic acid  $=2HIO(C_2,2NO_4,C_2H_2,C_8,C_2H)O_3, ^{\wedge}(C_{14}H_5)O_3$ , we let hydrosulphuric acid act, we obtain, by separation of sulphur, the so-called benzoic acid  $=2HIO(C_2,2NH_2,C_2H_2,C_8,C_2H)O_3, (C_{14}H_5)$



O<sub>3</sub>. In these double acids 2 at. H are replaced by 2NH<sub>2</sub>; hence they do not belong to the amin acids; also, when treated with acids they give no ammonia.

Since the radicals which contain H as the active element entirely agree in combining proportions with hydrogen, therefore, according to the principle of the organic radicals, they must, like hydrogen, unite with nitrogen in many proportions, and in like manner can in part substitute hydrogen even. And in fact compounds of methyl, ethyl, and amyl, with nitrogen exist, which correspond to ammonia and ammonium, and with these quite agree in chemical proportions. Thus NMe<sub>3</sub> corresponds to ammonia NH<sub>3</sub> and NMe<sub>4</sub> to ammonium NH<sub>4</sub>. The compound NMe<sub>4</sub> combines like ammonium with oxygen, sulphur, the halogens, &c. Thus ethyl gives with nitrogen NAe<sub>3</sub> and NAe<sub>4</sub>. If ammonia and bromethyl be placed together, the obtained product is (NH<sub>3</sub>Ae)Br—that is, bromide of ammonium, in which 1 atom of hydrogen is replaced by 1 atom of ethyl. If this salt be treated with potassa, we obtain bromide of potassium, water and NH<sub>2</sub>Ae, that is, ammonia, in which 1 atom of hydrogen is replaced by 1 atom of ethyl. If afterwards we let bromide of ethyl act upon this compound, we thus obtain a salt consisting of (NH<sub>2</sub>Ae<sub>2</sub>), that is, bromide of ammonium, in which 2 atoms of hydrogen are replaced by 2 atoms of ethyl. By treating with potassa we obtain NHAe<sub>2</sub>, and finally, by repeating this operation, NAe<sub>3</sub>. Like ethyl, behave methyl, amyl, benzid, tolid, etc. If we treat nitro-benzid (C<sub>12</sub>H<sub>5</sub>)NO<sub>3</sub> with hydrosulphuric acid, we obtain, with separation of sulphur, anilin NH<sub>2</sub>C<sub>12</sub>H<sub>5</sub>, that is, ammonia, in which 1 atom of hydrogen is substituted by 1 atom of benzid; in the same way arises toluidin NH<sub>2</sub>C<sub>14</sub>H<sub>7</sub> from nitrotolid; xylidin NH<sub>2</sub>C<sub>16</sub>H<sub>9</sub> from nitroxylid, and cumidin NH<sub>2</sub>C<sub>18</sub>H<sub>11</sub> from nitrocumid. It may, be also, that the organic radicals in these bases reciprocally exchange places; thence arises a great series, all of which answer to ammonia and ammonium, and, like those, give combinations which correspond to the imids, amids, and aminic acids, *e. g.*



If we subject oxalate of anilin=(NH<sub>3</sub>,C<sub>12</sub>H<sub>5</sub>)O; C<sub>2</sub>O<sub>3</sub> to distillation we obtain 2HO and oxanlid (NH,C<sub>12</sub>H<sub>5</sub>)C<sub>2</sub>O<sub>2</sub>=oxamid, and likewise corresponds benzanilid (NH,C<sub>12</sub>H<sub>5</sub>)C<sub>14</sub>H<sub>5</sub>O<sub>2</sub> to benzamid, NH<sub>2</sub>, C<sub>14</sub>H<sub>5</sub>O<sub>2</sub> and cumamilid (NH,C<sub>18</sub>H<sub>5</sub>)C<sub>18</sub>H<sub>7</sub>O<sub>2</sub> to cuminamid, aniloxa-



minic acid  $\text{HO}(\text{NH}, \text{C}_{12}\text{H}_5)^{\wedge} \text{C}_2\text{O}_3$  is likewise oxaminic acid  $\text{HO}(\text{NH}_2, \text{C}_2\text{O}_2)^{\wedge} \text{C}_2\text{O}_3$ .\*

If we let chlorine or bromine act upon these bases, substitutions take place, in consequence of which they lose the basic characteristics, and finally vanish entirely; thus we obtain, through the effects of chlorine upon anilin, three combinations corresponding to  $\text{NC}_{12}\text{H}_6\text{Cl}$ ,  $\text{NC}_{12}\text{H}_5\text{Cl}_2$  and  $\text{NC}_{12}\text{H}_4\text{Cl}_3$ ; the last is an entirely neutral body. These combinations correspond to the formulæ  $\text{NH}_2^{\wedge}(\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H})\text{Cl}_2$  and  $\text{NH}_2^{\wedge}(\text{C}_2\text{Cl}_2, \text{C}_8, \text{C}_2\text{H})\text{Cl}_2$ . By uniting the first combination with one atom anilin we obtain  $\text{NH}_2(2\text{C}_2\text{H}_2, \text{C}_8, \text{H}) + \text{NH}_2(\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H})\text{Cl}_2 = \text{NC}_{12}\text{H}_6\text{Cl}$ , and if the first combine with the second combination, thus arises  $\text{NC}_{12}\text{H}_4\text{Cl}_3$ ; these combinations are therefore double bases, corresponding to double acids.

In nature, bases are found which in their constitution entirely agree with the above named, as nicotin  $\text{NH}_2, \text{C}_{12}\text{H}_6$ , coniin  $\text{NH}_2, \text{C}_{16}\text{H}_{14}$ . All the bases of this class are volatile, in part gasiform, are absorbed in large quantities by water, and possess a strong ammoniacal smell.

Besides the above-mentioned basic combinations of nitrogen, other basic bodies occur in nature, which consist of nitrogen, carbon, hydrogen, and oxygen, and in their chemical relations behave the same as ammonia. Thus cinchonin consists of  $\text{NC}_{20}\text{H}_{12}\text{O}$ , quinin of  $\text{NC}_{20}\text{H}_{12}\text{O}$ , and aricin of  $\text{NC}_{20}\text{H}_{12}\text{O}_3$ . These bases saturate only one atom acid, whence it follows that the capacity of saturation is not dependent

\* However greatly the constitution of these bases corresponds to experience, by granting the entrance of hydrogen through the organic radicals, yet another opinion is defended, which, although perhaps less plausible, is worthy of consideration. All radicals which can substitute hydrogen contain H as an active element; when they combine with  $\text{C}_2$  we obtain the corresponding radicals of the negative group; thus methyl goes over into acetyl, benzid into benzoyl. If, instead of  $\text{C}_2\text{N}$  be taken, then goes over methyl  $\text{C}_2\text{H}_2\text{H}$  into  $\text{C}_2\text{H}_2\text{NH}$  and benzid into  $2\text{C}_2\text{H}_2\text{C}_8\text{NH}$ , thence we may consider these bases as hydrogenous compounds of nitrogen with the components  $\text{C}_2\text{H}_2$  in the hydroisocarbyls, and of the nucleus  $\text{C}_8$  in the hypopolycarbyls, therefore, is  $\text{Imid}=\text{NH}=\text{Methylimid}=\text{C}_2\text{H}_2, \text{NH}=\text{N}, \text{C}_8\text{H}_3$ ,

$\text{Amid}=\text{NH}_2=\text{Methylamid}=\text{C}_2\text{H}_2, \text{NH}_2=\text{N}, 2\text{C}_8\text{H}_3$ ,

$\text{Ammonia}=\text{NH}_3=\text{Methylammonia}=\text{C}_2\text{H}_2, \text{NH}_3=\text{N}, 3\text{C}_8\text{H}_3$ ,

$\text{Ammonium}=\text{NH}_4=\text{Methylammonin}=\text{C}_2\text{H}_2, \text{NH}_4=\text{N}, 4\text{C}_8\text{H}_3$ .

The bases  $\text{NH}_2, \text{C}_2\text{H}_3$ ;  $\text{NH}, 2\text{C}_2\text{H}_3$ ;  $\text{NH}, 3\text{C}_2\text{H}_3$  consist of  $\text{C}_2\text{H}_2, \text{NH}_3$ ;  $2\text{C}_2\text{H}_2, \text{NH}_3$ , and  $3\text{C}_2\text{H}_2, \text{NH}_3$ .

According to this view,

$\text{Ethylimid}=\text{C}_2\text{H}_2, \text{NH}$  and  $\text{benzidimid}=\text{C}_2\text{H}_2, \text{C}_8, \text{NH}$ .

$\text{Ethylamid}=\text{C}_2\text{H}_2, \text{NH}_2$  and  $\text{benzidamid}=\text{C}_2\text{H}_2, \text{C}_8, \text{NH}_2$ .

$\text{Ethylammonia}=\text{C}_2\text{H}_2, \text{NH}_3$  and  $\text{benzidammonia}=\text{C}_2\text{H}_2, \text{C}_8, \text{NH}_3$ .

\*  $\text{Ethylammonium}=\text{C}_2\text{H}_2, \text{NH}_4$  and  $\text{benzidammonium}=\text{C}_2\text{H}_2, \text{C}_8, \text{NH}_4$ .

$\text{Ethylamin}:\text{NH}_2, \text{C}_2\text{H}_5$  is then  $2\text{C}_2\text{H}_2, \text{NH}_3$ .

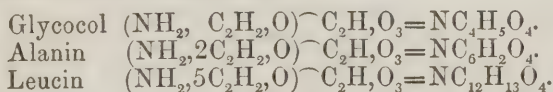
$\text{Biethylamin} \text{NH}, 2\text{C}_2\text{H}_5=\text{C}_2\text{H}_2, \text{NH}_3$  and  $\text{triethylamin} \text{N}, 3\text{C}_2\text{H}_5=\text{C}_2\text{H}_2, \text{NH}_3$ ; thus is the formula for anilin  $\text{NH}_2, \text{C}_{12}\text{H}_5=\text{C}_2\text{H}_2, \text{C}_8, \text{NH}_3$ ; the bases  $\text{NH}, \text{C}_2\text{H}_3, \text{C}_4\text{H}_5$  consist of  $3\text{C}_2\text{H}_2, \text{NH}_3=\text{C}_2\text{H}_2$  }  $\text{NH}_3$ , etc.  
 $2\text{C}_2\text{H}_2$

upon oxygen. It is very probable that these bases contain ammonia or methylamin, ethylamin, etc., combined with an organic oxide as a pairling. In these bases the physical characteristics are lost; if  $\text{NH}_3$  be taken as the active, then is the formula for cinchonin  $\text{C}_{20}\text{H}_9\text{O}, \text{NH}_3$ , for quinin  $\text{C}_{20}\text{H}_9\text{O}_2, \text{NH}_3$  and for aricin  $\text{C}_{20}\text{H}_9\text{O}_3, \text{NH}_3$ . Similar bases may be obtained artificially. Thus arises amarin through the action of ammonia upon oil of bitter almonds, furfuran by the action of ammonia upon furfural, etc. If we let the halogens react upon these bases, then arise substitutions similar to those mentioned above.

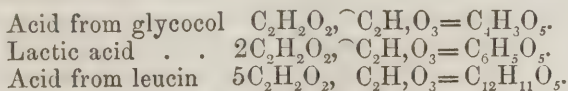
A peculiar group of combinations containing nitrogen which is connected in many relations with the above-mentioned organic bases, is formed by glyocol  $\text{NC}_4\text{H}_5\text{O}_4$ , alanin  $\text{NC}_6\text{H}_7\text{O}_4$ , and leucin  $\text{NC}_{12}\text{H}_{13}\text{O}_4$ . These bodies distinguish themselves especially by this, that they unite with bases, as well as with acids, and with the latter form paired combinations.

Glyocol, alanin, leucin, asparagin.

If we boil them with aqueous alkalies no ammonia is evolved, wherein they differ from the common amid combinations. If we bring alanin and nitrous acid together, we thus obtain, by the evolution of nitrogen gas, and the formation of water, lactic acid. Alanin has the same elementary constitution as lactamid; but this is a real amid combination, for, by treatment with alkalies, it goes over into ammonia and lactic acid. If we consider lactic acid as a paired acid  $\text{C}_4\text{H}_4\text{O}_2, (\text{C}_2\text{H})\text{O}_3$ , then lactamid consists of  $\text{NH}_2(\text{C}_4\text{H}_4\text{O}_2, \text{C}_2\text{H})\text{O}_2$ . If we take as a formula for alanin  $(\text{NH}_2, \text{C}_4\text{H}_4\text{O})\text{C}_2\text{H}_2\text{O}_3$ , it appears as a paired combination, whose pairling is  $\text{NH}_2, \text{C}_4\text{H}_4\text{O}$ . By the action of nitrous acid  $\text{NH}_2$  will be separated from the pairling, we obtain by oxidation  $\text{C}_4\text{H}_4\text{O}_2$  as a pairling associated with  $\text{C}_2\text{H}_2\text{O}_3$ , or lactic acid. The formulæ for these combinations are accordingly



It is very probable that, by the action of nitrous acid upon glyocol and leucin, acids are produced which behave to acetic and capronic acid as lactic acid does to metacetic acid.



In fact leucin, by heating with hydrate of potash, gives valerianic acid, under the evolution of ammonia. Asparagin also belongs to the same group; it gives with nitrous acid malic acid.

Asparagin consists of  $(\text{NH}_2, \text{C}_2\text{H}_2)\text{C}_2\text{H}_2\text{O}_3$ ; therefore the formula for malic acid is  $\text{C}_2\text{H}_2\text{O}, (\text{C}_2\text{H}_2)\text{O}_3$ . In the same manner as

nitrogen, do phosphorus, arsenic, and antimony (?) combine in many proportions with hydrogen; they all unite with  $H_3$ , forming compounds which correspond to ammonia. Phosphorus and arsenic are also known to form such compounds with one and two atoms hydrogen. These elements give quite analogous combinations with the radicals of the methyl group. Thus phosphorus gives with methyl  $PMe$ ,  $PMe_2$ , and  $PMe_3$ ; arsenic unites with two atoms methyl to form kakodyl  $=AsMe_2$ ; we are acquainted with combinations of antimony with three and with four atoms methyl, ethyl, and amyl  $=StMe_3, StMe_4; StAe_3, StAe^4; StAm_3$ . These bodies possess an enormous combining capacity; they unite directly with oxygen, sulphur, the halogens, &c. If we add iodmethyl to the compound  $StMe_3$ , we obtain a salt  $=StMe_4, I$ . If, instead of iodide of methyl, we take iodide of ethyl, thus arises  $StMe_3, AeI$ ; in like manner  $StAe_3$  gives with iodide of ethyl  $StAe_4, I$ . In this relation, these bodies behave completely analogous to ammonia and ammonium. In other respects, however, they differ entirely from ammonia; when the latter is brought in contact with chlorine gas, we obtain chloride of ammonium  $NH_3 + HCl = NH_4, Cl$ . Stibethyl  $StAe_3$ , on the contrary, brought in contact with the gas, evolves hydrogen gas, forming a combination which consists of one atom stibethyl and two atoms chlorine  $=StAe_3, Cl_2$ ; stibethyl forms combinations entirely corresponding with  $O_2, S_2, Br_2, I_2$ . These behave quite like metallic combinations; sulphur-stibethyl precipitates the metallic salts like sulphide of potassium. Kakodyl  $AsMe_2$  behaves like stibethyl; the compounds of kakodyl which correspond to the stibethyl compounds, contain only one atom O, S, Cl, Br, etc. Thence these radicals play a double part, acting as a metal and also as ammonia. That stibethyl should receive two atoms, and kakodyl in the corresponding compound only one atom O, S, Cl, etc., is sufficiently explained by granting that, in stibethyl, one atom ethyl forms with antimony a pairling, which unites with two atoms ethyl; its formula is then  $(StAe)^{\wedge}Ae_2$ ; the combining capacity is limited by the two atoms of ethyl which are found in active condition. Conformably to this, is the formula of kakodyl  $(AsMe)^{\wedge}Me$ .

Similar to the relations existing in the hydrocarbyls are those of the carbyls and azocarbyls, whose number is very insignificant. On the other hand there are a great number of organic combinations of which the rational formulæ, as yet, if we would not be lost in the sphere of hypothesis, cannot be accurately determined. Here belong especially the organic materials, which are found most widely diffused in nature.

According to the outward influences under which they are thrown, they divide into numerous products, whose radicals are the groundwork of the already-mentioned groups. Thus, sugar soon sepa-

Compounds of unknown constitution.

Common vegetable and animal matter.



rates, according to the activity of the fermentation and the degree of temperature, into carbonic acid and alcohol, or into lactic acid or butyric acid, under the evolution of hydrogen gas; thus wood fibrin gives, by dry distillation, many combinations of which none can be received as pre-existing. These products are formed by transposition of the elements. All these combinations belong to high orders; most of them contain many atoms of oxygen without one of them possessing the corresponding acid reaction. Many of them are found in all plants and animals, and are therefore called their proximate constituents. They decompose into *non-nitrogenous* and *nitrogenous*. The first consists of carbon, combined with hydrogen and oxygen in the same proportions as in water, wherefore many chemists have improperly called them carbon-hydrates. The greater number of them are isomeric, and may be converted into one another without suffering change in the elementary constitution; thus woody-fibrin, starch, caoutchouc, dextrin, milk-sugar, cane-sugar, all consist of  $C_{12}H_{10}O_{10}$ ; when they take the elements of 2 atoms water, they go over into fruit, or grape-sugar,  $C_{12}H_{12}O_{12}$ ; these combinations are, with the exception of milk-sugar, the main constituents of the vegetable kingdom. Also the nitrogenous compounds, as albumin, fibrin, casein, legumin, generally the protein compounds which occur in plants and animals, as well as in the tissues, furnishing glue and chondrin, which only occur in the animal body, stand in a relation to each other similar to that of the non-nitrogenous. These are combinations in which the elements are only combined by a weak affinity, and are therefore distinguished by the ease with which they are decomposed. These form the especial nutriment for the animal organization, and upon their mutability depends directly their physiological importance.

Besides the common compounds, a great number of substances occur, especially in the vegetable kingdom, which in respect to their extension do not belong to the common, Special vegetable matter. but agree with them in so far as they have a complicated constitution, and within certain limits separate into compounds of a lower order; they can be viewed as special vegetable matter. Generally, indeed, they are more permanent, and hence also they stand in another relation to the animal organization; very many of them are used in therapeutics. Most of these compounds possess weak acid properties, and many belong without doubt to the class of paired acids, as tannin, many of the so-called bitter principles, and most dyestuffs. Many colorless compounds possess the property, when they are exposed to the action of oxygen, together with ammonia, of going over into colored nitrogenous compounds, out of which the alkalies can no longer separate ammonia, and whose nature is not yet known, like phloridzin, orcin, etc.



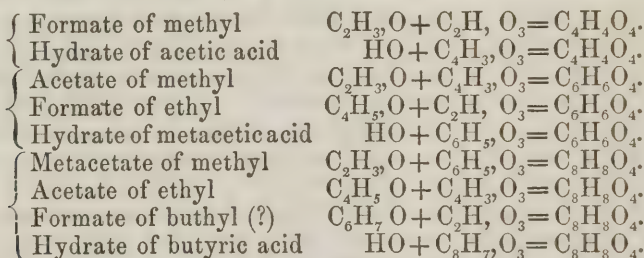
*Some general chemico-physical relations of the organic Combinations.*

Under metameric combinations, as was mentioned above, are

Metameric  
compounds  
of the methyl  
and formyl  
group.

understood those whose relative and absolute atomic number of the same elements are alike, but whose different properties are dependent upon the difference of the proximate constituents. Now since the radicals of the formyl group contain two more atoms of carbon

than the corresponding members in the series of the methyl group, and since the former with 3 at. oxygen form acids, the latter on the contrary with 1 at. oxygen form basic oxides, it is evident that by the crosswise union of the acids of the formyl series with the oxides of the methyl radicals, metameric compounds must arise, whose number must be increased by the corresponding acid hydrates. Thus, the following are metameric:—



The above are generally distinguished with:—

$A_1A_2A_3A_4A_5$ , the ascending members of the acids of the formyl series; farther, with

$B_1B_2B_3B_4B_5$ , “ “ “ “ “ oxides of the methyl series, and with

1 2 3 4 5, the corresponding members of the acids of the formyl series: thus we obtain the following series of metameric compounds:

$$A_1 + B_1 = 2.$$

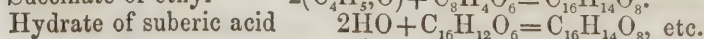
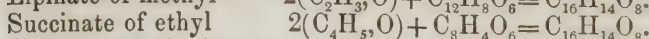
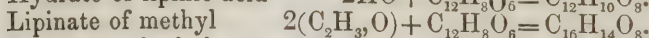
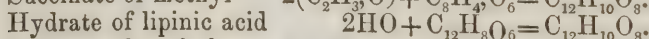
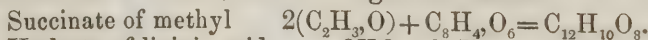
$$A_2 + B_1 = A_1 + B_2 = 3.$$

$$A_3 + B_1 = A_2 + B_2 = A_1 + B_3 = 4.$$

$$A_4 + B_1 = A_3 + B_2 = A_2 + B_3 = A_1 + B_4 = 4.$$

$$A_5 + B_1 = A_4 + B_2 = A_3 + B_3 = A_2 + B_4 = A + B = 6, \text{ etc.}$$

The acids of the hydropolycarbyls which belong to a group give the same metameric series, by their combinations with the above-mentioned bases. Thus, the following are metameric:—



It has been already remarked, in connection with the decomposition of organic compounds by heat, that generally the fluidity is dependent upon hydrogen, whilst carbon lessens it. Compounds containing a preponderance of hydrogen are at ordinary temperature either gaseous, or they boil at lower temperature, whilst those containing carbon in abundance are little volatile, or not at all so. But as the properties of the compounds of a higher order are at first determined by the proximate constituents, and not by the remote elements, so also in determining the boiling point, the influence exerted by the components whose individual elements are different must be determined. Thus, for example, the boiling point of acetyl  $C_2H_2, C_2H$ , depends, 1st, upon the influence of  $C_2H_2$  upon  $C_2H$ , and 2d, upon the influence of  $C_2$  upon  $H_2$  in  $C_2H_2$  and  $C_2$  upon  $H$  in  $C_2H$ ; in like manner, the boiling point of methyl  $C_2H_2, H$  depends upon the influence of  $C_2H_2$  upon  $H$ , and upon that of  $C_2$  upon  $H_2$  in  $C_2H_2$ . If the radicals combine with oxygen, the same circumstances are to be considered, and this is true also of the compounds of a higher order. Hydrate of metacetic acid  $HO(2C_2H_2, C_2H)O_3$  boils at  $140^\circ$  and hydrate of benzoic acid  $HO(2C_2H_2, C_8C_2H)O_3$  at  $240^\circ$ ; therefore the entrance of the nucleus  $C_8$  raises the boiling point  $100^\circ$ . Cinnamic acid  $HO, 2C_2H(2C_2H_2, C_8, C_2H)O_3$  boils at  $300^\circ$ ; hence the boiling point is raised from that of benzoic acid  $60^\circ$  by the addition of the pairing. The same difference is seen between benzin  $(2C_2H_2, C_8, H)H$ , and cinnamin  $2C_2H(2C_2H_2, C_8, H)H$ . If we compute the boiling point from the sum-total of the elements in such a way that we bring one into the computation as the most elevated, and the other as the lowest, we thus often obtain results which pass for a class of combinations, but cannot be transferred to others. Combinations which belong to one group, show in relation to their boiling points fixed regularity, whilst in proportion as the ascending member increases, the boiling point is raised an equal number of degrees; this elevation for  $C_2H_2$  amounts to from  $17$  to  $20^\circ$ . Hence, if the boiling point of the first member is known, we can compute very nearly that of the following members. Thus boil:—

		Found.
Wood-spirit . . . . .	$C_2H_4O_2$ at	$61^\circ$ .
Alcohol . . . . .	$C_4H_6O_2$ “	$78^\circ$ .
Amyl-spirit . . . . .	$C_{10}H_{12}O_2$ “	$133^\circ$ .
Formic acid . . . . .	$C_2H_2O_4$ “	$103^\circ$ .
Acetic acid . . . . .	$C_4H_4O_4$ “	$117^\circ$ .
Butyric acid . . . . .	$C_8H_8O_4$ “	$154^\circ$ .
Valerianic acid . . . . .	$C_{10}H_{10}O_4$ “	$172^\circ$ .
Benzin . . . . .	$C_{12}H_6$ “	$80^\circ$ .
Tolin . . . . .	$C_{14}H_8$ “	$108^\circ$ .
Cumin . . . . .	$C_{18}H_{12}$ “	$134^\circ$ , etc.

Indeed, great variations occur, which are probably dependent upon the rational formula.

**Hydrates.** The boiling point of the hydrate of oxide of ethyl (of alcohol)  $\text{AeO}, \text{HO}$ , lies at  $+78^\circ$ , and that of oxide of ethyl at  $+35^\circ$ ; accordingly, hydrate water raises the boiling point  $43^\circ$ . If we suppose that the boiling point of an organic hydrate is  $43^\circ$  higher than that of an anhydrous oxide, then is the boiling point of anhydrous formic acid  $103-43=60^\circ$ , and that of the

**Salt-like compounds.** following members  $18^\circ, 2.18^\circ, 3.18^\circ$  higher. The boiling point of acetate of ethyl is  $74^\circ$ ; it is hence about  $44^\circ$  lower than that of hydrate of acetic acid, and  $39^\circ$  higher than that of oxide of ethyl. Since only by the addition of  $\text{C}_2\text{H}_2$  the boiling point is raised  $18^\circ$ , that of the formate of ethyl must be  $74-18=56^\circ$ ; acetate of methyl must also have the same boiling point, which agrees with observation. It appears generally that metameric combinations of the same constitution have the same boiling point, so that the boiling point of an acid-hydrate is  $43^\circ$  higher than that of the corresponding ethyl combination, and  $61^\circ$  higher than that of the corresponding methyl combination.

**Oxides.** By oxidation, the boiling point of a compound is often very considerably raised, for example:—

{ Aldehyd . . . . .	$\text{HO}(\text{C}_4\text{H}_3)\text{O}$	boils at	$21^\circ$	} difference for $\text{O}_2=96^\circ$ .
{ Acetic acid . . . . .	$\text{HO}(\text{C}_4\text{H}_3)\text{O}_3$	"	$117^\circ$	
{ Chloral . . . . .	$\text{HO}(\text{C}_4\text{Cl}_3)\text{O}$	"	$94^\circ$	} " " $\text{O}_2=101^\circ$ .
{ Chlor-acetic acid . . . . .	$\text{HO}(\text{C}_4\text{Cl}_3)\text{O}_3$	"	$195^\circ$	
{ Butyral . . . . .	$\text{HO}(\text{C}_8\text{H}_7)\text{O}$	"	$95^\circ$	} " " $\text{O}_2=61^\circ$ .
{ Butyric acid . . . . .	$\text{HO}(\text{C}_8\text{H}_7)\text{O}_3$	"	$154^\circ$	
{ Valeral . . . . .	$\text{HO}(\text{C}_{10}\text{H}_9)\text{O}$	"	$110^\circ$	} " " $\text{O}_2=65^\circ$ .
{ Valerianic acid . . . . .	$\text{HO}(\text{C}_{10}\text{H}_9)\text{O}_3$	"	$175^\circ$	

The chlorine compounds of the primary radicals have generally a lower, and the bromine and iodine compounds a higher boiling point than the corresponding oxides. For example:—

Oxide of ethyl . . .	$(\text{C}_4\text{H}_5)\text{O}$	boils at	$35^\circ$ .
Chloride of ethyl . .	$(\text{C}_4\text{H}_5)\text{Cl}$	"	$11^\circ$ .
Bromide of ethyl . .	$(\text{C}_4\text{H}_5)\text{Br}$	"	$40^\circ$ .
Iodide of ethyl . . .	$(\text{C}_4\text{H}_5)\text{I}$	"	$70^\circ$ .

On the contrary, if a primary radical is converted into a derived, an elevation of the boiling point takes place, e. g.

{ Aldehyd . . . . .	$\text{HO}(\text{C}_4\text{H}_3)\text{O}$	boils at	$21^\circ$	} difference $73^\circ$ .
{ Chloral . . . . .	$\text{HO}(\text{C}_4\text{Cl}_3)\text{O}$	"	$94^\circ$	
{ Acetic acid . . . . .	$\text{HO}(\text{C}_4\text{H}_3)\text{O}_3$	"	$117^\circ$	} " $78^\circ$ .
{ Chlor-acetic acid . . . . .	$\text{HO}(\text{C}_4\text{Cl}_3)\text{O}_3$	"	$195^\circ$	
{ Chloride of acetyl . . . . .	$(\text{C}_4\text{H}_5)\text{Cl}_3$	"	$75^\circ$	} " $120^\circ$ .
{ Chloride of chloracetyl . . . . .	$(\text{C}_4\text{Cl}_3)\text{Cl}_3$	"	$195^\circ$	
{ Formate of ethyl . . . . .	$(\text{C}_4\text{H}_5)\text{O}, (\text{C}_2\text{H})\text{O}_3$	"	$55^\circ$	} " $41^\circ$ .
{ Chlor-formate of ethyl . . . . .	$(\text{C}_4\text{H}_5)\text{O}, (\text{C}_2\text{Cl})\text{O}_3$	"	$96^\circ$	

This example may be sufficient to show that regularity exists. It may be expected that after more exact observations we may be able to profit by the difference in the boiling points of different combinations in order to know their rational constitution; then it may also be possible to ascertain the influence which the individual components of a compound exert upon its boiling point.

The atomic volume, that is, the space which the compound atoms occupy in a combination, is found by dividing the specific gravity into the atomic weight of the compound, and, inversely, we obtain the specific gravity by dividing the atomic weight into the atomic volume. It may with greater probability be supposed that in the compounds of the same group, for each addition of  $C_2H_2$  the same increase of space takes place. But since the volume of a compound changes with the temperature, and a normal temperature for comparison is in fluid bodies unknown, all endeavors in this respect have been able to lead to no fixed laws. Only thus much has been established—that with much probability a regularity may be supposed to exist.

Atomic volume  
of organic com-  
pounds in the  
fluid state.

If we compare the atomic volume of such combinations as belong to a group, and differ from each other by  $+ \text{ or } - C_2H_2$ , we obtain for the entrance of  $C_2H_2$  a pretty constant number. The variations which have been observed are explained by the different temperatures at which the specific gravity was determined. Thus, if the atomic weight of oxygen = 100 be added, the atomic volume of wood-spirit  $HO, C_2H_3O = \frac{400}{0.798} = 500$ , and that of alcohol

$HO, C_4H_5O = \frac{575}{0.792} = 726$  at  $+ 20^\circ$ . The difference for  $C_2H_2$  is hence 226.

The atomic volume of amyl-spirit  $HO, C_{10}H_{11}O$  is at  $+ 16^\circ = \frac{1100}{0.818} = 1344$ . If we subtract the atomic volume of wood-spirit we obtain 844 for  $4C_2H_2$ , or 211 for  $C_2H_2$ . We obtain similar results in the acid-hydrates of the formyl group. Thus, the atomic volume of the hydrate of

Acetic acid  $HO, C_4H_3O_3 = \frac{750}{1.063} = 704$ , and that of the hydrate of

Formic acid  $HO, C^2H O_3 = \frac{575}{1.011} = 467$  difference for  $C_2H_2 = 237$ .

The atomic volume of valerianic acid is  $= \frac{1275}{0.937} = 1360$ . Now  $1360 - 467 = 893$  and  $\frac{893}{4} = 227$ . The results would, without



doubt, be more accordant if the specific gravity were determined at a normal temperature, e. g. at a boiling point. If, in relation to the atomic volume of fluid compounds a fixed law should be given, we would thus have a means of finding the specific gravity by computation.

Atomic volume of organic radicals and of their compounds in gaseous state. If we suppose that 1 atom hydrogen is equal to 2 volumes, then each atom of an organic radical in its gaseous state corresponds to 2 volumes of gas. The relative number of the individual atoms which form the organic molecule has no influence upon the atomic volume. 1 atom amyl =  $C_{10}H_{21}$  gives no more gas, according to the volume, than 1 atom methyl =  $C_2H_3$ . Hence, the specific gravity of these gases corresponds to the weight of the individual atoms of the radical. Therefore is:—

$$\text{Sp. gr. of methyl gas, } C_2H_3 = \frac{2.0,8360 + 3.0,1380}{2} = 1,0289.$$

$$\text{Sp. gr. of ethyl gas, } C_4H_5 = \frac{4.0,8360 + 5.0,1380}{2} = 2,0196.$$

$$\text{Sp. gr. of acetyl gas, } C_4H_3 = \frac{4.0,8360 + 3.0,1380}{2} = 1,8649.$$

If we consider methyl as consisting of  $C_2H_2, H$ , the active H appears as the volume-definer in the gaseous state; in like manner  $C_2H$ . If the organic radicals combine with oxygen, hydrogen, nitrogen, and the halogens, the same changes of volume occur as in the combinations of hydrogen with the elements. Thus are:—

(1 atom ethyl gas = 2 volumes + 1 atom oxygen gas = 1 volume) = 2 volumes oxide of ethyl gas.

(1 atom ethyl gas = 2 volumes + 1 atom chlorine gas = 2 volumes) = 4 volumes chlor-ethyl gas.

(1 atom benzid = 2 volumes + 1 atom hydrogen = 2 volumes) = 4 volumes benzin gas.

(1 atom acetyl = 2 volumes + 1 atom nitrogen = 2 volumes) = 4 volumes nitro-acetyl gas.

(1 atom oxide of ethyl = 2 volumes + 1 atom hydrogen = 2 volumes) = 4 volumes alcohol gas.

(1 atom acetyl = 2 volumes + 3 atoms oxygen = 3 volumes) = 2 volumes acetic acid gas.

(1 atom acetyl = 2 volumes + 3 atoms chlorine gas = 6 volumes) = 4 volumes chlor-acetyl gas, etc.

(Determination of the specific gravity of vapor of organic matter.)

Most of the organic compounds are colorless, yet there are also colored, as the organic dyestuffs, which also retain the color in their combinations.

The refracting power of organic fluids, when their constitution and density are the same, does not differ; but increases with the density of the substance (polymeric compounds). The fluid hydro-carbons of the same density have so much the greater refracting power as they contain more carbon. In fluids, which besides carbon and hydrogen, contain also oxygen, the refractive proportion and refractive power are the more striking, the less the capacity for oxygen, provided the density of the bodies is not different. In isomeric and metameric compounds of the same density, the refractive proportions are also identical.

Power of  
refraction.

By circular polarization is understood the power of many fluids, or matters dissolved in water, of bending the polarization plain of polarized rays of light which pass through these fluids, at a certain height of the fluid strata, some right, some left, whilst some pass unchanged. Often isomeric compounds, or those having the same constitution, have a different "rotation-power." Thus, the refractive power of turpentine oil is to the left, and that of lemon oil, of the same constitution, to the right. Sugar-cane, which bends to the right, is converted by fermentation, before separating into carbonic acid and alcohol, into uncrystallized sugar which bends to the left. It suffers the same changes by acids; the rapidity of the transposition is dependent upon the nature and quantity of the acid, as well as upon the temperature. Tartaric acid has, in a remarkable degree, the power of turning the plane of polarization to the right, whilst racemic acid of the same constitution does not change it. According to the latest researches, racemic acid consists of tartaric acid, and another acid isomeric with it, which bends polarized light to the left. Many bodies suffer from acids and bases, without being changed in their constitution, modifications whose difference can often be known only by the different refractive power. The rotation in solutions of the same substance, e. g. in solutions of sugar, is the stronger the more concentrated the solution is; hence we can use the strength of the refraction for determining the degree of concentration.

Circular  
polarization.

# SPECIAL PART.

## FIRST DIVISION.

### HYDROCARBYLS.

#### FIRST CLASS.

##### HYDROISOCARBYLS.

##### *First Group.*

The methyl group. Component  $C_2H_2$ ; Active element H.

The known members of the methyl group are:—

Member 1.	Methyl,	Me =	$C_2H_2, H = C_2H_3.$
"	2. Ethyl,	Ae =	$2C_2H_2, H = C_4H_5.$
"	4. Valyl,	Vy =	$4C_2H_2, H = C_8H_9.$
"	5. Amyl,	Am =	$5C_2H_2, H = C_{10}H_{11}.$
"	16. Cethyl,	Ce =	$16C_2H_2, H = C_{32}H_{33}.$
"	24. Cerossyl,	Co =	$24C_2H_2, H = C_{48}H_{49}.$
"	27. Cerotyl,	Cr =	$27C_2H_2, H = C_{54}H_{55}.$
"	30. Melissyl,	My =	$30C_2H_2, H = C_{60}H_{61}.$

A few chemical relations of this group.

As was stated in the General Part, the radicals of the methyl group quite agree in their chemical relations with hydrogen, which therefore is taken as the active element in the whole series. They combine with oxygen, sulphur, selenium, iodine, bromine, chlorine, and likewise with nitrogen, phosphorus, arsenic, and antimony, in the same atomic proportion as hydrogen, and possess, besides, the capability of uniting with hydrogen itself.

The oxides.

Of these radicals, the following are now known in an isolated condition: methyl, ethyl, valyl, and amyl. The oxides of these correspond to the formula  $RO$ , as  $MeO, AeO, AmO$ ; the lower members of the group are easily volatile; they possess a penetrating, etheric odor, and are little soluble in water; the higher members are solid at common temperatures, fat-like, fusible, and almost inodorous. The difference of boiling point between the individual members varies 18 to  $20^\circ$  for the addition of  $C_2H_2$ .

In their pure state, the oxides are indifferent; but they possess the capability, at the moment of their separation, of forming hydrates with water, and of uniting with all acids producing salt-like compounds. In this respect, the oxides are allied to the alkalies; the salt-like compounds appear more or less neutral, generally as the positive properties of the radicals excel those of the hydrogen; as follows from the basic combinations of nitrogen, in which the hydrogen is replaced by methyl or ethyl. The pure oxides are generally named ether (methyl-ether, wine-ether, amyl-ether), their hydrates are spirits (methyl-spirits, wine-spirits, amyl-spirits) and the salt-like combinations with acids, naphthæ, or compound ethers (acetic-ether, instead of acetate of oxide of ethyl).

The *Oxides* are always obtained from their hydrates, under co-operation of strong acids (sulphuric, phosphoric, and arsenic acid) and acid chlorides. For instance, if we bring alcohol  $\text{AeO}, \text{HO}$  and hydrate of sulphuric acid together, we obtain sulphate of ethyl  $\text{AeO}, \text{SO}_3$ . Production of the oxides. If this compound be heated to boiling with 2 to 3 atoms of water, the sulphuric acid unites with the water, whilst the volatile oxide of ethyl escapes gaseous; if, however, much water be present, we obtain alcohol; because the oxide of ethyl, at the moment of its liberation, combines with water (the detail is given under the individual compounds). The *Hydrates* agree in their physical properties with the pure oxides, yet the lower members, in particular, are miscible with water in every proportion; also the hydrate boils about  $44^\circ$  higher than the corresponding oxide. The oxyhydrates. In contact with potassium all the hydrates evolve hydrogen, under production of compounds of the oxides with anhydrous potassa  $\text{AeO}, \text{HO} + \text{K} = \text{KO}, \text{AeO} + \text{H}$ . In these compounds the organic oxides play the part of hydrate water; if they be brought in contact with water, they are in a moment decomposed; we obtain hydrate of potassa and oxyhydrate.

The *Salt-like Compounds*, with the *Strong Acids*, are mostly obtained by direct action of the latter upon the hydrates; generally, however, they form paired acids, which contain the neutral compound as pairing; thus is  $\text{AeO}, \text{HO} + 3\text{HO}, \text{SO}_3 = \text{HO}(\text{AeO}, \text{SO}_3) \sim \text{SO}_3 + 2\text{HO}, \text{SO}_3$ ; these are in aqueous solution easily decomposed into the hydrates and aqueous acids. With the weak acids we obtain the salt-like compounds, partly by double affinity ( $\text{AeO}, \text{SO}_3 + \text{KO}, \text{AcO}_3 = \text{AeO}, \text{AcO}_3 + \text{KO}, \text{SO}_3$ ), partly by introduction of hydrochloric acid gas into the spirit solution of the acids; in these cases the hydrochloric acid gas withdraws the hydrate water from the oxyhydrate, whilst the acid unites with the oxides. The salt-like compounds. The compounds with the weak acids are not easily soluble, or they are insoluble in water, and particularly in aqueous, alkali solutions, and they can even be shaken with



the last without suffering decomposition; the cause lies alone in the insolubility of the compounds in alkaline solutions. Decomposition, however, immediately follows the employment of an alcoholic potassa solution; since the acid unites with the potassa, the oxide combines with the hydrate water of the alkali. In general, the boiling point of the hydrate of the acid lies  $60^\circ$  higher than that of the corresponding methyl compound; thus hydrate of formic acid  $\text{HO}, \text{FoO}_3$  boils at  $105^\circ$ , and formate of methyl  $\text{MeO}, \text{FoO}_3$  at  $35^\circ$ ; by entrance of  $\text{C}_2\text{H}_2$  as well in the acids as in the bases, the boiling point rises 15 to  $20^\circ$ .

*Sulphur, Selenium, and Tellurium* combine with the radicals of the methyl group in several proportions, as with hydrogen and the alkali metals. The compounds with one atom sulphur behave like the sulphur bases; they give farther with hydrosulphuric acid paired acids, *e. g.*  $\text{H}(\text{AeS})\text{S}$ , which, on account of its powerful influence upon oxide of mercury, is named mercaptan (from mercurium captans); it is obtained by double affinity; so is  $\text{KS} + \text{AeO}, \text{SO}_3 = \text{AeS} + \text{KO}, \text{SO}_3$ ; farther,  $\text{KS}, \text{HS} + \text{AeO}, \text{SO}_3 = \text{H}(\text{AeS})\text{S} + \text{KO}, \text{SO}_3$ ; likewise is  $\text{KS} + \text{AeCl} = \text{AeS} + \text{KCl}$ . All the combinations of this class are distinguished by a highly disagreeable odor.

The haloid compounds correspond to the formulæ  $\text{RCl}, \text{RBr}, \text{RI}, \text{RFI}$ . They are obtained by the action of the gaseous hydrogen acids upon the oxyhydrates (*e. g.*  $\text{AeO}, \text{HO} + 2\text{HCl} = \text{AeCl} + 2\text{HO}, \text{HCl}$ ), or by the combined action of halogens and phosphorus upon those bodies [ $3(\text{AeO}, \text{HO}) + \text{P} + 3\text{I} = 3(\text{AeI}) + \text{PO}_3 + 3\text{HO}$ ]. In general, the chlorine compounds boil  $24^\circ$  lower than the corresponding oxides, the bromine compounds  $2^\circ$ , and the iodine  $35^\circ$  higher.

All the radicals of this group correspond to 2 volumes gas:  
 Atomic proportions of this group in form of gas. Methyl gas =  $\text{C}_2\text{H}_3$ , sp. gr. of  $\text{C}_2 = 2.0, 8360 = 1.6725$   
 " "  $\text{H}_3 = 6.0, 0693 = 0.4158$   
 " "  $\text{C}_2\text{H}_3 = 2\text{vol.} = 2.0883$

Specific gravity of gas. It follows the sp. gr. of methyl gas =  $\frac{2.0883}{2} = 1.044$ .

For each addition of  $\text{C}_2\text{H}_2$  the sp. gr. of the gases is increased  $0.8360 + 2 \cdot 0.0693 = 0.9746$ .

The Oxides of these groups correspond of course to 2 vols. gas:

2 volumes methyl gas = 2.0883

1 " oxygen " = 1.1093

= 2 volumes gaseous oxide of methyl = 3.1974. Sp. gr. = 1.5982.

The Oxyhydrates are equal to 4 volumes gas:

2 volumes gaseous oxide of methyl = 3.1974

+ 2 " " hydrogen = 1.2479

= 4 volumes gaseous hydrate = 4.4353. Sp. gr. = 1.1037.

The *Salt-like Compounds of the Oxides* are equal to 4 volumes gas = 2 volumes gaseous oxide of methyl + 2 volumes oxygen gas.

The *Sulphur Compounds* correspond to 2 volumes gas:

2 volumes gaseous methyl	= 2.0883
+ $\frac{1}{3}$ " " sulphur	= 2.2140
= 2 " " sulphide of methyl	= 4.3023. Sp. gr. = 2.1511.

The *Haloid Compounds* are equal to 4 volumes gas:

2 volumes gaseous methyl	= 2.0883
+ 2 " " chlorine	= 4.8800
= 4 " " chloride of methyl	= 7.9683. Sp. gr. = 1.9921.

The *Hydrogen Compounds* are equal to 4 volumes gas:

2 volumes gaseous methyl	= 2.0883
+ 2 " " hydrogen	= 0.1386
= 4 " " hydromethyl	= 2.2369. Sp. gr. = 0.5567.

The increase of the sp. gr. for the ascending members is given from the above.

#### FIRST MEMBER.

*Methyl*: Me:  $C_2H_2, H = C_2H_3$ .

*Occurrence and Production.* Methyl is found in the oil of the *Gaultheria procumbens* as oxide of methyl combined with salicylic acid. It is formed by decomposition of the hydrate of acetic acid, by dry distillation of wood, particularly beech wood, by putrefaction of organic bodies, etc., simultaneously with other products.

*Methyl*: Me. We submit a concentrated solution of acetate of potassa to the electric current; at the negative pole hydrogen is evolved, and at the positive a mixture of Methyl. carbonate of methyl and methyl gas. If the mixture be shaken with potassa and with sulphuric acid, the pure methyl remains behind. Methyl is also obtained by action of potassium upon nitroacetyl under production of cyanide of potassium  $(C_2H_2, C_2H)N + K = (C_2H_2H) + K, NC_2$ . Colorless gas, insoluble in water, of slight etheric odor, completely indifferent toward sulphuric acid, sulphur, and iodine. 100 vol. alcohol absorb 113 vol. gas.

*Hydro-Methyl* (marsh gas),  $MeH$ , is found in mire of swamps, and is produced by the putrefaction of organic substances, particularly of fossil-coal, with carbonic acid, as also by the dry distillation of most organic bodies, particularly at high temperature. It is obtained pure if a mixture of two parts crystallized acetate of soda, two parts hydrate of potassa, and three parts lime, be heated and the gas received over water.  $HO(C_2H_2, C_2H)O_3 = (C_2H_2, H)H + 2CO_2$ . Colorless, inodorous, and tasteless gas, indifferent, and burning with slightly luminous flame. By chlorine, and admission of light,

Compounds of methyl with hydrogen (marsh gas).

it is decomposed with an explosion; in the dark, we obtain first chloride of methyl ( $C_2H_3Cl$ ), then terchloride of formyl ( $C_2HCl_3$ ), and at last terchloride of chlorformyl ( $C_2ClCl_3$ ).

*Oxide of Ethyl* (wood-ether):  $MeO$ . One part pure wood-spirit (oxyhydrate of methyl) is submitted to distillation with two parts concentrated sulphuric acid and the evolved gas conducted first through water, then through potassa solution, and finally through a tube filled with chloride of calcium. The gaseous methyl oxide thus purified is received over mercury. It is colorless, of an etheric odor, burns with a blue flame, and is not yet liquid at  $-12^\circ$ . One measure of water at  $18^\circ$  absorbs 37 measures of the gas, and acquires thereby an etheric odor and pepper-like taste. It is dissolved in large quantity by wood-spirit, alcohol, ether, and concentrated sulphuric acid; if the sulphuric acid solution be mixed with water, the gas escapes with a hiss. In contact with chlorine, methyl oxide is converted by degrees into  $C_2H_3O + (C_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$ ;  $(C_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$  and at last into  $(C_2Cl) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$ .

*Oxyhydrate of Methyl* (wood-spirit):  $MeO, HO$ . The aqueous fluid, obtained by dry distillation of the beech-wood, and which is a mixture of water, acetic acid, wood-spirit, mesit, xylit, and acetate of methyl, besides other empyreumatic products (named crude wood-spirit), is a few times distilled over quicklime, and the pure wood-spirit thus obtained is completely saturated with fused chloride of calcium. After some days the mixture is completely distilled over the water-bath, and the residue, which is a compound of wood-spirit, with chloride of calcium, is submitted to distillation with water; the liberated wood-spirit, which passes over, is, for complete purification, yet several times rectified over quicklime. Very mobile, colorless fluid, miscible with water and ether in every proportion, of peculiar aromatic odor and burning taste; sp. gr. = 0.798 at  $20^\circ$ , boils at  $63^\circ$ . Taken internally it intoxicates like alcohol, is a solvent of ethereal oils, gums (varnishes), and generally behaves in these respects like alcohol; burns with feeble flame.

With *Baryta* and *Chloride of Calcium* it gives definite chemical combinations =  $BaO(MeO, HO)$  and  $CaCl, (MeO, HO)$ .

If the *vapor* of *wood-spirit* be conducted over a heated mixture of hydrate of potassa and quicklime, it is decomposed into formic acid and hydrogen gas. In a pure state it suffers no change in the air; but if its vapor, mixed with air, be conducted over platinum black, formic acid is produced, accompanied by great evolution of heat; *oxidizing acids* produce the same decomposition; mixed with nitrate of silver it produces a precipitate consisting of formate and nitrate of silver. By distillation with *water*, *per-oxide of manganese*, and

*sulphuric acid*, we procure formate of methyl and methylal. *Chloride of lime* converts the wood-spirit into terchloride of formyl ( $C_2HCl_3$ ); chlorine decomposes it with violence; as final product there remains an oily fluid, which consists of  $C_6H_3Cl_3O_2 = (C_2Cl)O, HO + (C_2H_2)Cl_3 = (C_2H) \left\{ \begin{array}{l} O \\ Cl \end{array} \right. + (C_2H_2)Cl_3$ .

*Carbonate of Methyl*:  $MeO, CO_2$ , is in a pure state unknown.

*Sulphocarbonate of Methyl*:  $MeO, CS_2$ . If a solution of iodine in wood-spirit be added to an aqueous solution of methyloxide-sulphocarbonate of potassa, oily drops are deposited, which consist of  $MeO, C_2S_4O$ . But if finely pulverized iodine be added to a solution of the salt mentioned, there is separated, by heating, sulphide and iodide of potassium, accompanied by copious evolution of gas, whilst there is found upon the surface a brown fluid, which, by repeated rectification, leaves pure sulphocarbonate of methyl;  $(MeO, CS_2 + KO, CS_2) + I = MeO, CS_2 + KI + CO + S$ . Thin-flowing yellow liquid, of strong aromatic odor and sweetish taste; sp. gr. = 1.143; boils at  $170^\circ$ , insoluble in water, easily soluble in alcohol and ether. Mixed with an alcoholic solution of potassa, after a few hours carbonate of potassa is deposited, and in the solution is found sulpho-methylhydric acid  $MeS, HS$ . *Chlorine* gas decomposes the compound; we obtain in diffused light, a beautiful crystallizing body.

*Basic Borate of Methyl*:  $3MeO + BoO_3$ . Chloride of boron is conducted into wood-spirit so long that a copious evolution of hydrochloric acid follows. The basic borate of methyl which is deposited is removed and purified by repeated distillation. Water-clear very thin fluid of 0.955 sp. gr.; boils at  $72^\circ$ , and possesses a penetrating odor like wood-spirit; burns with a green flame, and in contact with water decomposes into wood-spirit and boracic acid. *Acid borate of methyl*:  $MeO, 2BoO_3$ . Anhydrous pulverized boracic acid is distilled with an equal quantity of pure wood-spirit until the temperature rises to  $110^\circ$ , the wood-spirit which has gone over being repeatedly poured back into the retort. The residue in the retort is ground, digested twenty-four hours with anhydrous ether, and the etheric solution distilled until the boiling point rises to  $200^\circ$ . The residue is the pure combination; it appears a transparent glassy mass, which is soft by heating, and can be drawn into threads. Burns with green flame, and, in contact with water, instantly decomposes into wood-spirit and boracic acid, accompanied by strong heat.

*Nitrate of Methyl*:  $MeO, NO_3$ . Equal parts nitrate of potassa and wood-spirit are gently warmed in a retort with 2 parts hydrate of sulphuric acid; when the reaction begins, the nitrate of methyl distils over without external heat. This is purified by cautious distillation over chloride of calcium and oxide of lead. Colorless, neutral fluid, boiling at  $66^\circ$ , of sharp, etheric odor, and which is



easily soluble in alcohol and ether, but not easily in water; burns with yellow flame, and at  $150^{\circ}$  explodes with great violence.

*Sulphate of Methyl*:  $\text{MeO}, \text{SO}_3$ . We conduct anhydrous gaseous oxide of methyl into a dry balloon, containing sulphuric acid—or we distil a mixture of 1 part wood-spirit with 8 to 10 parts sulphuric acid. The oily distillate is washed with warm water, then brought in contact with a little chloride of calcium, and at last rectified over quicklime. Colorless, oily fluid, of garlic-like odor, which in contact with water decomposes into wood-spirit and methyloxyd-sulphuric acid  $\text{MeO}, \text{HO}, 2\text{SO}_3$ . In contact with anhydrous ammonia, it forms a white crystalline mass, the *sulphomethylan*  $= \text{NH}_3 + \text{MeO}, \text{SO}_3$ .

*Sulphomethyl-sulphuric Acid*:  $\text{HO}(\text{Me}, \text{SO}_2) \text{SO}_3$ , is obtained by the action of dilute nitric acid upon sulphide of methyl and hydrogen ( $\text{MeS}, \text{HS}$ ), upon bisulphide of methyl and sulphocyanide of methyl, simultaneously with some sulphuric acid. To remove the nitric acid, the solution is evaporated upon the water bath; the residue is dissolved in water, the solution saturated with carbonate of baryta, and the fluid, filtered from the sulphate of baryta, evaporated to crystallization. The obtained crystals of sulphomethyl-sulphate of baryta are dissolved in water, and the baryta precipitated by sulphuric acid; by evaporation of the solution separated from the sulphate of baryta, the hydrate of the acid is obtained. If sulphochlor-formylchlorid-sulphuric acid  $\text{HO}, (\text{C}_2\text{Cl}), \left\{ \begin{smallmatrix} \text{Cl} \\ \text{SO}_2 \end{smallmatrix} \right\} \text{SO}_3$  at the moment of its separation, be brought in contact with water, and if at the same time a body be present which takes away the chlorine, we thus obtain, first, sulphoformylechloride-sulphuric acid,  $\text{HO}, (\text{C}_2\text{H}) \left\{ \begin{smallmatrix} \text{Cl} \\ \text{SO}_2 \end{smallmatrix} \right\} \text{SO}_3$  and then sulphomethyl-sulphuric acid. Zinc dissolves in sulphochlor-chlorformyl-sulphuric acid without evolution of gas; the same is produced by the galvanic current when amalgamated zinc plates serve as electrodes. A thickish inodorous fluid, very acid, and which bears a high temperature without suffering decomposition. The acid forms with all the bases salts soluble, neutral, and easily crystallizable.

*Methyloxyd-carbonic Acid*:  $\text{HO}(\text{MeO}, \text{CO}_2) \text{CO}_2$ . If carbonic acid be conducted into a solution of anhydrous baryta in wood-spirit, methyloxyd-carbonate of baryta separates and is washed with wood-spirit. The salt is easily soluble in water, but it soon decomposes under separation of carbonate of baryta. This acid is not known in an isolated condition.

*Methyloxyd-chlorcarbonic Acid*:  $\text{HO}(\text{MeO}, \text{CO}_2) \text{C} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix} \right\}$  is obtained by the action of oxychlor-carbonic acid  $\text{C} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix} \right\}$  upon wood-spirit:  $\text{MeO}, \text{HO} + 2(\text{COCl}) = (\text{MeO}, \text{CO}_2) \text{COCl} + \text{HCl}$ . A colorless,

very thin, volatile fluid, of penetrating odor, and sinking in water. Gives with ammonia a crystallizable deliquescent product, *urethylan* =  $\text{MeO}, \text{CO}_2 + \text{NH}, \text{CO}$ .

*Methyloxyd-sulphocarbonic Acid*:  $\text{HO}(\text{MeO}, \text{CS}_2) \text{CS}_2$ . The potassa salt of this acid is obtained by dissolving sulphocarbonic acid ( $\text{CS}_2$ ) in a wood-spirit solution of potassa. Its crystals are feather like and of a silver lustre.

*Methyloxyd-sulphuric Acid*:  $\text{HO}(\text{MeO}, \text{SO}_3) \text{SO}_3$ . A mixture of 2 parts sulphuric acid, and 1 part wood-spirit is diluted with water and afterwards saturated with carbonate of baryta. From the solution filtered from sulphate of baryta, the remaining baryta is accurately precipitated by sulphuric acid, and the fluid separated from the precipitate is evaporated in a vacuum. The acid crystallizes in white needles easily soluble in water, but not easily in alcohol; it tastes acid, and gives with all the bases salts soluble in water, and which contain water of crystallization. By warming the aqueous solution the acid decomposes into wood-spirit and sulphuric acid; the salts leave, after being strongly heated, a sulphuric acid salt.

*Protosulphide of Methyl*:  $\text{MeS}$ . A disagreeably smelling fluid, sinking in water, is obtained by distillation of  $\text{KS}$  with  $\text{MeO}, \text{SO}_3$ . Gives with chlorine

Compounds of methyl and sulphur.

at last  $(\text{C}_2\text{Cl}) \begin{cases} \text{S} \\ \text{Cl}_2 \end{cases}$ .

*Sulphocarbonate of Sulphide of Methyl*:  $\text{MeS}, \text{CS}_2$ . We distil  $\text{KS}, \text{CS}_2$  with  $\text{MeO}, \text{SO}_3$ . Colorless, very disagreeably smelling fluid of 1.159 sp. gr.; boils at  $204^\circ$ ; is scarcely soluble in water, but in all proportions miscible with alcohol. Bromine decomposes the compound under the production of  $(\text{C}_2\text{H}) \begin{cases} \text{S} \\ \text{Br}_2 \end{cases}, \text{CS}_2 + \text{MeS}, \text{CS}_2$ .

*Bisulphide of Methyl*:  $\text{MeS}_2$ . Bisulphide of potassa is distilled with methyloxyd-sulphate of lime  $\text{CaO}, (\text{MeO}, \text{SO}_3) \text{SO}_3$ . Clear, colorless liquid, of intolerable odor; sp. gr. 1.046; boiling point =  $116^\circ$ ; miscible in all proportions with ether and alcohol; scarcely soluble in water.

*Tersulphide of Methyl*:  $\text{MeS}_3$ . We distil quinque-sulphide of potassium with methyloxyd-sulphate of lime; at the beginning  $\text{MeS}_2$  goes over, and at  $200^\circ$   $\text{MeS}_3$ . Quite equals the foregoing compound.

*Methyl-hydrosulphuric Acid* (methyl-mercaptan):  $\text{H}(\text{MS}) \text{S}$ . A mixture of equal parts  $\text{KO}, (\text{MeO}, \text{SO}_3) \text{SO}_3$  and  $\text{KS}, \text{H}_2\text{S}$ , dissolved in a little water, is submitted to distillation; the distillate is shaken with potassa; the fluid separated from the potassa solution is dried over chloride of calcium. A light, very disagreeably smelling fluid, which boils at  $21^\circ$ , and unites with oxide of mercury, into  $\text{Hg}(\text{MeS})\text{S}$  under great evolution of heat. Gives with dilute nitric acid sulphomethyl-sulphuric acid.

Paired combinations of protosulphide of methyl.

*Iodide of Methyl*:  $\text{MeI}$ . A solution, not too concentrated, of

Combinations of methyl with the halogens. iodine in wood-spirit is shaken with some phosphorus until the color of iodine vanishes; the fluid is poured off from the phosphorus, and in it more iodine is dissolved; the iodine solution is again shaken with phosphorus, and the operation continued until the solution fumes copiously. It is necessary always to keep the vessel cool. After twenty-four hours the solution, separated from phosphorus, is submitted to distillation. To the distillate iodine is added, in small quantities, so long as the color vanishes. Afterward, it is all shaken with water, and the deposited iodide of methyl is deprived of water over chloride of calcium. An extremely mobile fluid; flows from a glass, like quicksilver; of disagreeable odor, and 2.199 sp. gr.; boils at  $43.8^{\circ}$ , burns with difficulty under emission of violet vapor; chlorine forms chloride of methyl under separation of iodine. An alcoholic solution of iodide of methyl gives immediately, with nitrate of silver, a precipitate of iodide of silver.

*Bromide of Methyl:* MeBr, is obtained like the iodine compound. Colorless, neutral, strongly smelling fluid of 1.664 sp. gr., boils at  $13^{\circ}$ , and is yet fluid at  $-13^{\circ}$ .

*Chloride of Methyl:* MeCl: 2 parts common salt, 1 part wood-spirit, and 3 parts hydrate of sulphuric acid, are submitted to distillation, and the evolved gas received over water. Colorless gas of etheric odor; is still gaseous at  $-18^{\circ}$ ; 1 volume water dissolves 2.5 volumes, and assumes a sweet etheric odor. If the gas be conducted over heated potassa, we thus obtain chloride of potassium and formate of potassa. Chlorine decomposes chloride of methyl, forming  $\text{MeCl} + (\text{C}_2\text{H})\text{Cl}_3$ ;  $(\text{C}_2\text{H})\text{Cl}_3$  and  $(\text{C}_2\text{Cl})\text{Cl}_3$ .

*Fluoride of Methyl:* MeFl. Colorless gas of agreeable etheric odor; 1 volume water absorbs 1.6 volume gas.

#### SECOND MEMBER.

*Ethyl:*  $\text{Ae} = 2\text{C}_2\text{H}_5$ ,  $\text{H} = \text{C}_4\text{H}_9$ .

*Occurrence and Production.*—Neither ethyl nor compounds of it has yet been found in nature; it is always a product of the vinous fermentation which consists of the conversion of fruit or grape sugar into alcohol (oxyhydrate of ethyl) and carbonic acid.

*Ethyl:*  $\text{Ae} = 2$  volumes gas. If iodide of ethyl with zinc be heated to  $150^{\circ}$ , in a tube closed by fusion, we obtain iodide of zinc, ethyl hydroethyl (?), and elayl:  $3(\text{AeO}, \text{I}) + 3\text{Zn} = 3\text{ZnI} + \text{Ae} + \text{AeH} + \text{C}_4\text{H}_9$ . If the tube be opened under mercury, hydroethyl and elayl are first evolved, and afterward ethyl. Colorless gas, smelling slightly like ether; burns with luminous flame; is at  $-18^{\circ}$  still gaseous, but, by the pressure of  $2\frac{1}{2}$  atmospheres at  $3^{\circ}$ , it is converted into a colorless fluid, very mobile; 1 volume alcohol absorbs 18.13 volumes gas; insoluble in water. Under the co-operation of light it combines with chlorine and bromine; the nature of these compounds is not yet known.



*Hydroethyl*:  $\text{AeH}=4$  volumes gas, arises simultaneously with ethyl and elayl by the decomposition of iodide of ethyl by zinc. Also, by decomposition of nitrometacetyl by potassium, as well as by decomposition of iodide of ethyl by zinc, in the presence of water, the same compound appears to be obtained. Colorless gas, insoluble in water.

Compounds of ethyl with hydrogen.

*Oxide of Ethyl* (ether):  $\text{AeO}=2$  volumes gas. A mixture of five parts of alcohol and nine parts sulphuric acid is submitted to distillation in a retort. What goes over at first is mostly alcohol, and is removed. When the boiling point rises to  $140^\circ$ , through the tubulus, by means of a glass tube, we introduce alcohol in such proportion that the temperature remains constant. Ether and water distil over; since ether is volatile, care must be taken for the purpose of condensation. The distillate consists of two layers, the upper, which is a mixture of much ether with alcohol and a little water, is shaken with milk of lime and afterward distilled by gentle heat upon water bath. To remove the alcohol the distillate is shaken with water, then the withdrawn ether once more distilled, and at last rectified over chloride of calcium (theory of the formation of ether, see ethyloxydsulphuric acid). Also ether is obtained by the action of phosphoric acid, arsenic acid, fluoboron and acid chlorides upon alcohol. Pure ether is a very thin-flowing, colorless fluid, of penetrating, agreeable odor, and sharp, burning and afterward cooling taste. It boils at  $35^\circ$  and is, on account of its volatility, easily inflammable; even at ordinary temperatures it evaporates rapidly under production of considerable cold; stiffens at  $-44^\circ$  to a white crystalline mass; sp. gr. = 0.697. Ether dissolves many inorganic salts, particularly chlorides of the metals, as bichloride of mercury, of gold and iron; farther, organic acids containing little oxygen, as benzoic, cinnamic, and salicylic acids, most gums, caoutchouc, and the volatile oils. 100 parts ether take up eight parts of sulphur and 2.6 parts phosphorus. If etheric vapor be inhaled, it produces, after a little time, complete insensibility. If the vapor be conducted through a glowing tube, we obtain elayl gas, marsh gas, aldehyd and acetal; if these be brought in contact with heated mixture of *hydrate of potassa* and *quicklime*, we obtain, under the production of carbonate of potassa, marsh gas (hydro-methyl) and hydrogen:  $2\text{AeO} + 3\text{HO} = \text{MeH} + \text{H}_4 + 2\text{CO}_2$ . If ether be a long time preserved in a vessel containing air, it forms, at first, acetate of ethyl, and later, acetic acid. All bodies which easily yield oxygen convert ethyl into acetyl. If ether fall drop-wise upon a brick heated to  $150^\circ$ , a blue appearance is observed, whilst a gaseous mixture is produced, strongly exciting the eyes, and consisting of carbonic acid, aldehyd, acetic acid and water, etc. The same products arise, also, if etheric vapor, by means of a wick, be brought in contact with a red-hot, coiled,

Ethyl and oxygen.

Properties of ether.

Decomposition of ether.



platina wire; the wires glow so long as ether is present (aphlogistic lamp). *Nitric acid* decomposes ether under production of carbonic, acetic, and oxalic acid. If it be dropped upon *Chromic acid* it inflames, and the acid is decomposed. If ether be distilled with chromate of potassa, or peroxide of manganese and sulphuric acid, acetic acid is produced. *Chlorine* converts ether by degrees into the

following compounds:  $(C_4H_5)O + (C_4H_3) \left\{ \begin{array}{l} O \\ Cl_2 \end{array} \right. ; (C_4H_3) \left\{ \begin{array}{l} O \\ Cl_2 \end{array} \right. ; (C_4H_3) \left\{ \begin{array}{l} O \\ Cl \end{array} \right. + (C_2Cl_2, C_2H) \left\{ \begin{array}{l} O \\ Cl_2 \end{array} \right. ; (C_2Cl_2, C_2H) \left\{ \begin{array}{l} O \\ Cl_2 \end{array} \right. (C_4Cl_3) \left\{ \begin{array}{l} O \\ Cl_2 \end{array} \right. \quad Be-$

sides it forms, as secondary products, chloride of ethyl, aldehyd, chloral, etc. Bromine completely decomposes ether, little by little, under production of hydrobromic acid, bromide of ethyl, bromal, etc. Iodine dissolves abundantly in ether; after a little time the solution contains hydriodic acid.

*Oxyhydrate of Ethyl* (Alcohol):  $AeO, HO = 4$  volumes gas. The whiskey occurring in commerce, which is obtained by distillation of different fermented liquors, is a mixture of water, alcohol, and different so-named fusel-oles. By repeated distillations of whiskey we obtain the so-called spiritus or alcohol, which contains 80 to 85 per cent. spirits of wine. The last portion of water can be absorbed from alcohol only by chemically-acting bodies, partly on account of the affinity of alcohol for water, partly because water also, below its boiling point, passes over in a gasiform condition. To obtain alcohol as free as possible from water the former is rectified over well-burnt charcoal to remove the fuseloles, then left standing a few days with coarsely broken, fused chloride of calcium, and at last, by distillation, the anhydrous alcohol is obtained. (Effloresced Glauber's salts, slight-burnt gypsum, quicklime, etc., answer the purpose not so completely as chloride of calcium. Sommering's method of removing water by animal membrane. Apparatus for obtaining alcohol from fermented liquors by one distillation.)

*Anhydrous Alcohol* is a water-clear very thin-flowing liquid, of agreeable, penetrating odor and burning taste. Sp. gr. = 0.7947 at 15°, boils at 78°, and at -98° is converted into a solid. Alcohol mixes with water, wood-spirit, and ether, in all proportions. In the anhydrous state it operates, both externally and internally, as a poison. Spirited into the blood it produces death, by coagulation of the blood. Diluted with water and drank in large quantities it occasions intoxication. It is on account of its volatility very inflammable. Alcohol combines with many neutral chlorides of metals, as *chloride of magnesium, calcium, and manganese*, and accepts in these compounds the place of water of crystallization. With *chloride of tin*, it gives partly doughy and partly solid, crystalline

Combinations  
of oxide of  
ethyl with wa-  
ter, alcohol.

Properties of  
alcohol.

Compounds of  
alcohol.

compounds, which decompose at high temperatures, and produce ether and chloride of ethyl. It behaves in the same way to *perchloride* of iron, *chloride* of antimony, arsenic, zinc, aluminium, etc. Sulphur and phosphorus are dissolved by alcohol in small quantity; the latter dissolves farther hydrate of potassa and of soda, most chlorides and bromides of metals, the organic acids, oils, gums (alcohol varnish), the fats, the different sugar-like substances, all the organic bases; most oxygen salts with inorganic acids (except nitrate of magnesia and lime), caoutchouc, starch, the proteine compounds, etc., are insoluble in alcohol.

*Water and Alcohol* mix, under condensation and evolution of heat. The diminution of volume continues until 53.73 volumes alcohol are combined with 49.836 volumes Alcohol and water. water; the mixture then takes, at 15°, the space of 100 volumes. Its sp. gr. = 0.927, and it contains 1 atom alcohol to 6 atoms water. If more water be added to the mixture an apparent expansion occurs. Hence it follows that a mixture of alcohol and water cannot correspond to the mean specific gravity of both. By direct determination, the following specific gravity for such mixtures, at 15°, has been found—according to the volume per cent. The boiling point of such mixtures rises with the addition of water.

Amt. alcohol.	Sp. gr.	Boil. pt.	Amt. alcohol.	Sp. gr.	Boil. pt.
100	0.7947	78°.	40	0.9523	95°
90	0.8368	78°.15	30	0.9656	97°
80	0.8645	83°.75	20	0.9740	98°
70	0.8907	88°.50	10	0.9880	98°.75
60	0.9141	91°.25	0	1.0000	100°
50	0.9348	93°.75			

By the mixture of 2 parts alcohol with 1 part snow, the temperature is reduced always in proportion as the alcohol is stronger. By employing alcohol of 99 per cent. Alcohol and snow. the thermometer falls to 25°; by 70 per cent. to 18°; by 50 per cent. to 16°, and by 20 per cent. to 8°.

*Wines* contain very different quantities of alcohol. Madeira 20 per cent., Xeres 20 per cent., Malaga 16 per cent., Bordeaux 15 per cent., strong Rhenish wine 10 to 12 per cent., good Bavarian beer 3 to 4 per cent., common brandy 40 to 50 per cent., Cogniac 50 to 60 per cent., rum about 60 per cent., arak 70 per cent., etc. Amount of alcohol in a few spirituous drinks.

*Alcohol and ether* mix in all proportions. If such a mixture be shaken with a concentrated solution of easily soluble salts, the ether is again separated. A mixture of 1 part ether, and 2 to 3 parts alcohol, is known under the name of *Liquor Anodynus Hoffmanni*. By powerful voltaic

Alcohol and ether.

Decomposition  
of alcohol.

action upon alcohol the hydrate water is decomposed, the hydrogen going to the negative pole and the oxygen to the positive; the galvanic decomposition is more intense if a little anhydrous potassa be dissolved in the alcohol. The decomposition of the alcohol into its proximate *constituents*, setting the ether free, follows only by the co-operation of oxygen; and in most cases, before the separation follows, combinations are formed of ether with the acting body. Upon the behavior of *hydrate of sulphuric acid* v. ether-sulphuric acid. *Anhydrous sulphuric acid* produces, at ordinary temperatures, with water-free alcohol, simple sulphate of ethyl; if the action, however, is intensive, the alcohol is decomposed under production of different bodies, as althionic and ethionic acid, etc. Upon the conversion of alcohol into acetic acid v. the latter. If alcohol be distilled with *peroxide of manganese* and *dilute sulphuric acid*, formic and acetic acid, aldehyd, and ether go over. *Nitric acid* acts powerfully upon alcohol, producing aldehyd, nitrite of ethyl, acetic and oxalic acid. By the action of acid *nitrate of silver* or of *mercury*, fulminating salts arise. *Concentrated chloric acid* acts with great violence upon alcohol, often producing inflammation, under formation of acetic and hydrochloric acid; *bromic acid* behaves in the same manner. *Dry chromic acid*, brought into a mixture of air and alcoholic vapor, causes an explosion. *Chlorine* and *bromine* convert alcohol at first into aldehyd and then into *chloral* and *bromal*; distilled with *chloride* or *bromide of lime* we obtain chloride or bromide of formyl. If *iodine* be brought into an alcoholic solution of potassa, iodide of formyl is produced. As for the rest, the decompositions of alcohol equal those of ether.

Combinations  
of oxide of  
ethyl with  
acids.

*Carbonate of Ethyl*:  $\text{AeO}, \text{CO}_2$ . Sodium is, little by little, added to oxalate of ethyl ( $\text{AeO}, \text{C}_2\text{O}_3$ ) until no farther evolution of carbonic acid takes place. The mass remaining behind is mixed with water, and the carbonate of ethyl which separates is rectified over sodium. Colorless, easily-flowing liquid, of burning aromatic taste; sp. gr. = 0.975; boils at  $126^\circ$ . Brought together with aqueous ammonia, oxide of ethyl forms alcohol and *Ether-oxamid* ( $\text{AeO}, \text{CO}_2$ ) $\text{NH}_2$ ,  $\text{CO}$ . *Chlorine* decomposes ether under production of carbonate of oxychloride of chloracetyl ( $\text{C}_4\text{H}_3$ )  $\left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 \end{array} \right.$ ,  $\text{CO}_2$ .

*Sulphocarbonate of Ethyl*:  $\text{AeO}, \text{CS}_2$ . Ether-sulphocarbonate of potassa (v. below) is with alcohol stirred round, and gradually iodine is added so long as the color vanishes; iodide of potassium is deposited, and over it is found a yellow fluid, which, after evaporation, leaves crystals which consist of  $\text{AeO}, \text{C}_2\text{S}_4\text{O} = \text{AeO}_2, 2\text{C}_2\text{S}_2$ , and can be named *Ethylbioxyd-sulphocarbonic Acid*. If these crystals, upon which hydrochloric acid itself does not act, are distilled in an oil bath at  $200^\circ$ , thus sulphocarbonate of ethyl passes



over; simultaneously carbonic acid is evolved, and, as residue, remains a solid mass consisting of  $C_2S_4$ :  $2(AeO_2, 2CS_2) = 2(AeO, CS_2) + CO_2 + CS_4$ . Light yellow, clear liquid, of not very disagreeable odor and sweetish taste; it mixes with alcohol and ether in all proportions; sp. gr. 1.07; boiling point  $200^\circ$ .

*Borate of Ethyl.* With boracic acid oxide of ethyl gives two compounds,  $3AeO + BO_3$  and  $AeO, 2BoO_3$ , which are obtained quite like the corresponding methyl compounds, and agree with the latter in properties. With silicic acid, oxide of ethyl unites in three proportions, forming  $3AeO + SiO_3$ ,  $3AeO + 2SiO_3$  and  $3AeO + 4SiO_3$ . The first compound is obtained by the action of chloride of silicium upon absolute alcohol; it presents a colorless fluid of etheric penetrating odor and pepper-like taste, and which boils at  $162^\circ$ , mixes with alcohol and ether in every proportion, but is insoluble in water. The second and the third combination are obtained by the action of chloride of silicium upon alcohol, to which 1 atom water is added. The compound  $3AeO, 2SiO_3$  distils over at  $350^\circ$ ; it appears as a colorless fluid of slight odor and taste; the combination  $3AeO, 4SiO_3$  remains behind as a glass-like mass, which is soft at  $100^\circ$ , and in strong heat divides into  $3AeO, 2SiO_3$  and  $2SiO_3$ .

*Phosphite of Ethyl:*  $2HO, AeO, PO_3$ , is obtained by the action of  $PCl_3$  upon alcohol under simultaneous production of hydrochloric acid and chloride of ethyl. The obtained fluid is evaporated in a vacuum containing pieces of potassa. Syrup-thick acid fluid, which, however, is a mixture of phosphorous and hydrochloric acid with the ethyloxid compound. With bases it gives salts, which are easily decomposed in the watery solution, and consist of  $(HO, MO, AeO), PO_3$ .

*Tribasic Phosphate of Ethyl:*  $3AeO + PO_5$ , is obtained by distillation of biether-phosphate of lead. Water-clear fluid, of agreeable etheric odor; boils at  $142^\circ 5$ .

*Bi-ether-phosphate of Ethyl:*  $HO, 2AeO + PO_5$ . By the action of anhydrous phosphoric acid upon ether or alcohol we obtain two compounds  $= HO, 2AeO + PO_5$  and  $2HO, AeO + PO_5$ . If the mixture diluted with water be saturated with oxide of lead we obtain an easily soluble salt, and one not easily soluble; the first corresponds to the formula  $PbO, 2AeO, PO_5$ . By decomposition of these salts with sulphuric acid, and evaporation in a vacuum, we obtain the pure compound as a syrup-thick mass. The lead salt crystallizes in needles of a silky lustre, soluble in water; it fuses at  $180^\circ$ , and stiffens to a crystalline mass.

*Ether-phosphoric Acid (Phosphorinic Acid:*  $2 HO, AeO, PO$ . Syrup-thick phosphoric acid is mixed with an equal weight of anhydrous alcohol, the mixture after a little time dissolved in 8 parts of water, and completely saturated with carbonate of baryta. From the solution filtered from the phosphate of baryta, after the



removal of the still boiling alcohol, the baryta is precipitated by sulphuric acid and by evaporation in a vacuum, the compound is obtained as a syrup-thick fluid of very sour, biting taste. It dissolves in water, alcohol, and ether in all proportions, and gives with bases soluble combinations, which consist of  $2\text{MO}, \text{AeO}, \text{PO}_5$ .

*Ether-sulpho-phosphoric Acid*:  $2\text{HO}, \text{AeO}, \text{P} \left\{ \begin{smallmatrix} \text{O}_3 \\ \text{S}_2 \end{smallmatrix} \right.$  is obtained by the action of  $\text{PO}_3\text{S}_2$  upon alcohol; gives with bases salts which consist of  $2\text{MO}, \text{AeO}, \text{P} \left\{ \begin{smallmatrix} \text{O} \\ \text{S}_2 \end{smallmatrix} \right.$ .

*Nitrate of Ethyl*:  $\text{AeO}, \text{NO}_3$ . If hypo-nitrous acid be conducted into alcohol, there goes over a pale yellow fluid of agreeable odor, like that of apples, and of sweet burning taste. This fluid is received into a well-refrigerated vessel; sp. gr. 0.886; boils at  $21^\circ$ ; becomes sour by itself after a little time in a well-closed vessel. If we let hydro-sulphuric acid act upon the combination, we obtain, under a separation of sulphur, water, alcohol, and ammonia,  $\text{AeO}, \text{NO}_3 + 6\text{HS} = 6\text{S} + 2\text{HO} + \text{AeO}, \text{HO} + \text{NH}_3$ . If a mixture of equal quantities of alcohol and dilute nitric acid be distilled, we obtain the so-named *spiritus nitri dulcis*, which is a mixture of aldehyd, hyp-nitrite of ethyl, and alcohol; simultaneously also carbonic acid and cyanogen are formed.

*Nitrate of Ethyl*:  $\text{AeO}, \text{NO}_5$ . We distil 1 volume nitric acid of 1.40 sp. gr. with 2 volumes alcohol, and from 1 to 2 per cent. urea, which decomposes the formed hyponitrous acid. Colorless, agreeably smelling fluid, insoluble in water, boils at  $85^\circ$ ; sp. gr. = 1.112. Decomposes at a high temperature under violent explosion. Hydrosulphuric acid acts upon this combination as upon the former.

*Sulphite of Ethyl*  $\text{AeO}, \text{SO}_2$ , is obtained by the action of  $\text{S}_2\text{Cl}$  upon alcohol. Colorless fluid, of peculiar etheric odor, and first cooling then burning taste; boils at  $160^\circ$ ; sp. gr. = 1.085.

*Sulphate of Ethyl*:  $\text{AeO}, \text{SO}_3$ . Vapor of anhydrous sulphuric acid is conducted into refrigerated ether. The syrup-thick mass obtained is shaken with water and ether; the latter dissolves the sulphate of ethyl which remains behind after evaporation in a vacuum. Yellow oil-like fluid of sharp taste, like oil of peppermint, of 1.120 sp. gr.; distillable only in a current of air. By heating with water decomposes into ether-sulphuric, methionic, and isæthionic acid.

*Hyperchlorate of Ethyl*:  $\text{AeO}, \text{ClO}_7$ . An intimate mixture of ether-sulphate of baryta with hyperchlorate of baryta is submitted to distillation, yet the temperature not raised above  $170^\circ$ . Transparent colorless fluid of agreeable odor and taste. Explodes with great violence by heating, rubbing, and by shaking, nay often without external cause.

*Sulphethyl-sulphuric Acid*:  $\text{HO}, (\text{AeSO}_2)^-\text{SO}_3$ , arises by the

action of dilute nitric acid upon bisulphide of ethyl, hydrosulphate of ethyl (mercaptan) and upon sulphocyanide of ethyl. Also, it is obtained by the combined action of hydrochloric acid and chlorate of potassa upon sulphocyanide of ethyl. The production is the same as that of sulphomethyl-sulphuric acid. Heavy oily fluid, in which after a time colorless crystals are formed; it possesses a strong acid taste, which afterwards reminds of the odor of hydro-phosphoric acid; inodorous, soluble in water and alcohol in all proportions; bears a high temperature without suffering decomposition. With all bases it forms soluble salts which have a great tendency to crystallize. Many contain water of crystallization, which they often first lose far above  $100^{\circ}$ . It is best obtained by decomposition of the baryta salt with the corresponding sulphuric acid salts.

*Ether-carbonic Acid*:  $\text{HO}(\text{AeO}, \text{CO}_2)\text{CO}_2$ . It is only known in combination with potassa. Into a refrigerated solution of hydrate of potassa, in absolute alcohol, carbonic acid is conducted. After a little time a mixture of carbonate and ether-carbonate of potassa is precipitated, which latter is dissolved by absolute alcohol. If the solution be mixed with ether, the potassa salt is precipitated in leaflets of mother-of-pearl lustre. Water decomposes the compound immediately into alcohol, carbonic acid, and carbonate of potassa.

*Etheroxyd-chlorcarbonic Acid*:  $(\text{AeO}, \text{CO}_2)^{\sim}\text{C} \begin{Bmatrix} \text{O} \\ \text{Cl} \end{Bmatrix}$ , is obtained by the action of oxychlor-carbonic acid  $\text{COCl}$  upon anhydrous alcohol. After the reaction has taken place, the obtained liquid is shaken with water, and the separated compound purified over chloride of calcium and oxide of lead. Transparent colorless liquid of agreeable odor; the gas mixed with air suffocates and excites to tears in a high degree; insoluble in water, soluble in alcohol, sp. gr. 1.33, boils at  $94^{\circ}$ . Brought together with aqueous ammonia, we obtain *urethran*  $(\text{AeO}, \text{CO}_2)\text{NH}_2\text{CO}$ . This is soluble in water and alcohol, and crystallizes in large regular crystals.

*Ether-sulpho-carbonic Acid*:  $\text{HO}, (\text{AeO}, \text{CS}_2)^{\sim}\text{CS}_2$ . To a solution of potassa, in absolute alcohol, little by little, so much sulpho-carbonic acid is added that the fluid becomes neutral. This is then cooled to  $0^{\circ}$ , at which temperature the potassa salt is crystallized out. A concentrated solution of this salt, in a high cylinder glass, is decomposed by sulphuric acid, and then so much water added that the acid can separate; it is purified by repeated shaking with cold water. Oil-like, colorless, peculiar smelling fluid, of feebly sour and later astringent taste; heavier than water, reddens at first litmus, very inflammable, and decomposes at  $24^{\circ}$  into alcohol and sulpho-carbonic acid. It drives carbonic acid out of its combinations; the compounds, with the alkalies, are soluble, those with oxides of heavy metals insoluble.

*Sulphocarbonate of Bioxide of Ethyl* (ethylbioxysulphocarbonate):  $\text{AeO}, \text{C}_2\text{S}_4\text{O} = (\text{AeO}_2\text{CS}_2)^{\sim}\text{CS}_2$  (?). This combination, whose

production was given above at sulphocarbonate of ethyl, crystallizes in white shining prisms, of mustard-like taste; melts at  $28^{\circ}$ , and decomposes at  $160^{\circ}$ , in the way already specified. If dry ammonia gas be conducted into an alcoholic solution of the compound, and the introduction be broken when the deposition of sulphur is terminated, we obtain, after evaporation, ether-sulphocarbonate of ammonia, and an oil-like body, *Hanthogenamid*  $C_6H_7N S_2O_2 = (NH_2, CO)^{\wedge} AeO, CS_2$ , which from the etheric solution is obtained, by the addition of some alcohol, in heavy crystals, which are not easily soluble in water, but easily soluble in alcohol and ether. The alcoholic solution gives precipitates with chloride of platinum and bichloride of mercury; the first consists of  $PtCl_2, C_6H_7NS_2O_2 + PtCl, C_6H_7NS_2O_2$ . Potassa solution decomposes the compound into alcohol and sulphocyanic acid. At  $150^{\circ}$  it decomposes into a colorless fluid, smelling like mercaptan and cyanic acid, and whose alcoholic solution gives, with perchloride of mercury, a precipitate consisting of  $Hg(AeS)S + HgCl$ .

*Ether-sulphuric Acid:*  $HO(AeO, SO_3)SO_3$ . Equal atoms of alcohol and hydrate of sulphuric acid are quickly mixed together, whereby a perceptible elevation of temperature takes place, in which case the production of ether-sulphuric acid follows in a moment (the same goes slowly on at a low temperature). The mixture then contains 1 atom ether sulphuric acid, 2 atoms free alcohol, and  $3HO + SO_3$ ; it is diluted with eight times its weight of water, completely saturated with carbonate of baryta, and the baryta of the ether-sulphate of baryta solution, filtered from the sulphate of baryta, is accurately precipitated by sulphuric acid. The filtered solution of ether-sulphuric acid is left standing in a vacuum over sulphuric acid until the specific gravity of the acid is 1.319. Oily colorless fluid, of sharp acid taste, which mixes in all proportions with water; by heating, the watery solution decomposes, according to the concentration, either into sulphuric acid and ether or alcohol. If the acid be heated by itself, over an oil bath to  $100$  to  $140^{\circ}$ , it decomposes into ether and hydrous sulphuric acid; more strongly heated it decomposes, under formation of sulphurous acid, ether-sulphate of elayl, elayl, carbonic acid, etc. With *bases* the ether sulphuric acid gives neutral salts, soluble in water, which mostly contain water of crystallization; many of these lose their water by heating, without suffering decomposition; also can the water of a few be removed by boiling with alcohol. If the aqueous solution of the salt be a long time boiled, it decomposes into alcohol and sulphuric acid salts; they all contain 1 atom base, and are obtained either direct or by double elective affinity.

Upon the decomposition of ether-sulphuric acid into sulphuric acid and ether, is founded the ordinary production of ether. As was given above a mixture of equal atoms of hydrate of sulphuric acid and alcohol, consists of 1 atom ether sulphuric acid, 2 atoms alcohol, and 1

Theory of the  
production of  
ether.



atom  $3\text{HO} + \text{SO}_3$ . If this mixture be submitted to distillation, at first alcohol goes over, and if the temperature be raised to  $100^\circ$  the acid decomposes into ether, which escapes gaseous, and sulphuric acid, which diffuses in the water present; if we suppose the decomposition has completely taken place, the residue must consist of  $3\text{SO}_3 + 4\text{HO}$ . But if the temperature rises above  $140^\circ$ , before all the ether-sulphuric acid is decomposed, the sulphuric acid which becomes free decomposes the ether, and we obtain sulphurous acid, elayl, wine-oil, whilst a black mass, the *Thiomelanic Acid*, remains behind. When the temperature has risen to  $140^\circ$ , if we let alcohol slowly flow into the boiling fluid, in such a manner that the temperature remains constant, the alcohol is immediately decomposed into ether and water; this division follows, without doubt, from the affinity of sulphuric acid for water; the latter is taken up by the sulphuric acid, whilst the ether escapes. But in proportion as the alcohol flows thereto, the quantity of water increases, and now ether and water pass over together in the proportions as in alcohol. The production of ether, therefore, can no longer be explained by the attraction of sulphuric acid for water. Sulphuric acid seems, at a high temperature, to exert a similar, of course quite unknown, influence upon alcohol, as yeast does upon the fermentation of sugar. The simultaneous escape of ether and water, some believe they can explain, by the opinion that the water vanishes in the vapor of ether; but this opinion is inadmissible, because, in any case, so much water is present that alcohol must be immediately reproduced. If it should yet be known that ether, at  $140^\circ$ , has not the capability, at the moment of its liberation, to combine with water into alcohol, the difficulty of the theory will thus be removed; besides, it is to be considered that, in alcohol, ether and water have a very feeble affinity.

*Simple Sulphide of Ethyl*:  $\text{AeS}$ , is obtained like the simple sulphide of methyl. A very thin-flowing liquid of penetrating odor, like *assafetida*, burns with blue flame; boils at  $75^\circ$ , sp. gr. 0.825, gives with chlorine by degrees  $(\text{C}_2\text{H}_2, \text{C}_2\text{H}) \left\{ \begin{matrix} \text{S} \\ \text{Cl}_2 \end{matrix} \right.$  and  $(\text{C}_2\text{Cl}_2, \text{C}_2\text{Cl}) \left\{ \begin{matrix} \text{S} \\ \text{Cl}_2 \end{matrix} \right.$  Combination of ethyl with sulphur, selenium, and tellurium.

*Sulphocarbonate* of sulph-ethyl  $\text{AeS}, \text{CS}_2$ . Slightly yellow fluid, heavier than water, easily soluble in ether and alcohol; possesses a garlic-like sweetish odor, and an agreeable, very sweet, anise-like taste. Is produced like the corresponding methyl compound. *Bisulphide of Ethyl*:  $\text{AeS}_2$ . Tersulphide of potassium is distilled with ether-sulphate of potassa, the distillate repeatedly washed with water and rectified over chloride of calcium. At  $150^\circ$ , the pure compound goes over. Completely colorless fluid, of strong garlic odor, and penetrating, sharp, afterward sweet taste, sp. gr.=1.60; boils at  $152^\circ$ . Gives, treated with nitric acid, sulph-ethyl-sulphuric acid. Tersulphide of ethyl (Thialole)  $\text{AeS}_3$ .



Quite resembles the former compound, and is obtained by distillation of quinque-sulphide of potassa with ether-sulphate of potassa.

*Selen-ethyl*:  $\text{AeSe}$ , is obtained, like simple sulphide of ethyl, with which it quite agrees in properties.

*Tellur-ethyl*:  $\text{AeTe}$ , is obtained, if tellur-potassium be distilled with ether-sulphate of potassa and some water. Yellow-red liquid, heavier than water, of strong, highly disagreeable odor long continued; poisonous, boils below  $100^\circ$ , burns with white flame under diffusion of a thick white vapor of tellurous acid. Is decomposed by nitric acid with violence, and if hydrochloric acid be added to the obtained solution, a heavy colorless liquid separates.

*Ethyl-hydrosulphuric Acid* (Mercaptan):  $\text{H}(\text{AeS})\text{S}=4$  volumes gas. A saturated solution of  $\text{KS,HS}$  is mixed with a concentrated solution of ether-sulphate of potassa, and the whole distilled upon the water bath. The distillate is shaken with a small quantity of oxide of quicksilver, and afterwards deprived of water by chloride of calcium. Colorless, extremely thin-flowing, etheric fluid, of highly disagreeable smell and odor, miscible in all proportions with alcohol and ether, and little soluble in water; is converted, by strong refrigeration, into a greasy mass. It dissolves only a little sulphur and phosphorus; is very inflammable, and burns with a blue flame. Does not react acid, boils at  $36^\circ$ , sp. gr. = 0.835. With oxide of nitrogen mercaptan forms a red smoking fluid; treated with dilute nitric acid it is converted into sulph-ethyl-sulphuric acid; as a mean product we obtain  $\text{AeS,SO}_2$ . With oxides of the metals, particularly with oxide of mercury, mercaptan combines with great violence under production of water and metal combinations, in which the hydrogen of the acid is replaced by the metal, the alkali metals are converted into the same compound accompanied by evolution of hydrogen.

*Potassium-sulph-ethyl*:  $\text{K}(\text{AeS})\text{S}$  appears as a white, granular, shining mass, easily soluble in water; the combinations with heavy metals are with difficulty soluble in water, but several are easily soluble in alcohol. The *Mercury compound*  $\text{Hg}(\text{AeS})\text{S}$  crystallizes from the alcoholic solution in white transparent leaves, which in a dry condition have a silver lustre. The *Silver compound* appears as a snow-white mass. All the metal compounds are decomposed by hydrosulphuric acid, accompanied by production of sulpho-metal and mercaptan, from which it follows that they cannot be ordinary compounds of sulpho-metals with  $\text{AeS}$ .

*Ethyl-selen-hydric Acid*:  $\text{H}(\text{AeSe})\text{Se}=4$  volumes gas, is obtained like the former compound, under the employment of  $\text{KSe,H Se}$ . Colorless, highly disagreeable smelling fluid, heavier than water, in which it is insoluble; boils at  $100^\circ$ , easily inflammable, and burns with intense blue flame, under formation of selenious acid and

vapor of selenium. Behaves towards the metals like the former compound.

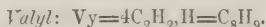
*Iodide of Ethyl*:  $\text{AeI}=4$  volumes gas, is obtained like iodide of methyl. Colorless fluid, strongly refracting light, of penetrating etheric smell, miscible in all proportions with alcohol and ether; boils at  $70^\circ$ ; sp. gr. 1.9755. Decomposes, by conduction through a glowing tube, into iodide of elayl. Nitric acid precipitates iodine; chlorine forms chloride of elayl under deposition of iodine. Distilled with concentrated solution of potassa it is partly converted into iodide of acetyl. An alcoholic solution of iodide of ethyl with nitrate of silver gives immediately iodide of silver. After a little time is yellow.

*Bromide of Ethyl*,  $\text{AeBr}=4$  volumes gas, is produced like bromide of methyl. Water, clear, etheric smelling fluid of sweet taste; boils at  $40^\circ.7$ ; sp. gr.  $=1.473$ ; suffers no change in the air.

*Chloride of Ethyl* (hydrochloric ether):  $\text{AeCl}=4$  volumes gas. Absolute alcohol, completely saturated by hydrochloric acid gas, is gently warmed in a flask, which is connected by a gas-evolving tube with two bottles. In the first bottle is water of  $25^\circ$  to  $30^\circ$ , under which the tube passes; the second is placed in a cold mixture. In the first, the hydrochloric acid and alcohol remain behind; in the second, the chloride of ethyl collects. Colorless, extremely mobile liquid of aromatic odor; boils at  $12^\circ.5$ ; sp. gr.  $0.874$ ; dissolves in 50 parts water; miscible in all proportions with ether and alcohol. Chloride of ethyl gives with *Anhydrous Sulphuric Acid* an oily combination; it farther combines with *Chloride of Tin* and *Antimony*, and *Perchloride of Iron*, forming crystalline masses which are immediately decomposed in contact with water. An alcoholic solution of potassa decomposes the compound, under the production of chloride of potassium and alcohol. Treated with *chlorine*, acetyl is converted by degrees into the following compounds:  $(\text{C}_2\text{H}_2, \text{C}_2\text{H})\text{Cl}_3 + (\text{C}_4\text{H}_5)\text{Cl} = \text{C}_4\text{H}_4\text{Cl}_2$ ;  $(\text{C}_2\text{H}_2, \text{C}_2\text{H})\text{Cl}_3 = \text{C}_4\text{H}_3\text{Cl}_3$ ;  $(\text{C}_2\text{Cl}_2, \text{C}_2\text{H})\text{Cl}_3 + (\text{C}_4\text{H}_3)\text{Cl}_3 = \text{C}_4\text{H}_2\text{Cl}_4$ ;  $(\text{C}_2\text{Cl}_2, \text{C}_2\text{H})\text{Cl}_3 = \text{C}_4\text{HCl}_5$ ;  $(\text{C}_2\text{Cl}_2, \text{C}_2\text{Cl})\text{Cl}_3 = \text{C}_4\text{Cl}_6$ .

*Fluoride of Ethyl*:  $\text{AeFl}$ . Very volatile, colorless fluid of garlic-like odor; burns with a blue flame under evolution of acid vapor.

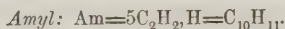
#### FOURTH MEMBER.



By electrifying a well-cooled, saturated solution of valerianate of potassa, we obtain hydrogen at the negative pole ending in a copper plate; and, at the positive pole, terminating in a platinum plate (if both are separate from each other by a porous septum), carbonic acid, valylen (butyren gas),  $\text{C}_8\text{H}_8$  and an oily fluid which consists of valyl  $\text{C}_8\text{H}_9$ , and valerianate of valyl (?)  $(\text{C}_8\text{H}_9)\text{O}, (\text{C}_{10}\text{H}_9)$

O<sub>3</sub>. If this fluid be boiled with an alcoholic solution of potassa, so that the vapor formed flows back again, thus separates valerianate of potassa, but which by continued boiling must again vanish. If the fluid after cooling be mixed with much water, we obtain valyl in the form of a light etheric fluid, which boils at 108°, smells agreeably aromatic, mixes in every proportion with ether and alcohol, burns with very sooty flame, and possesses at 18° a specific gravity=0.694. Density of its vapor=2 volumes gas. *Dilute Nitric Acid* does not act upon valyl; concentrated seems to convert it into butyric acid. *Dry Chlorine gas*, decomposes valyl by the access of light, under the production of hydrochloric acid; at last a pasty mass remains; Bromine acts in a similar manner. As valyl forms from valerianic acid, so *Propyl* C<sub>6</sub>H<sub>7</sub> forms by decomposition of butyric acid.

## FIFTH MEMBER.



*Occurrence and Production.*—Amyl seems to be formed by a process of fermentation. It is found as oxyhydrate of amyl in fuselole of potato whiskey, as well as in that of wine; it is farther obtained by electrical decomposition of capronate of potassa KO, (C<sub>12</sub>H<sub>11</sub>)O<sub>3</sub>.

Amyl.

*Amyl:* Am = 2 volumes gas. Like iodide of ethyl, iodide of amyl decomposes (if, in a closed tube, with zinc amalgam, it be heated to 160—180°), accompanied by production of iodide of zinc, into amyl, hydro-amyl, and valeren C<sub>10</sub>H<sub>10</sub>. By distillation, a mixture of hydro-amyl and valeren first passes over, and at 155° the so-called amyl. Colorless, transparent fluid, of slightly etheric odor and burning taste. At —30° it is thick, but not solid; boils at 155°; sp. gr. 0.7704; does not inflame at ordinary temperatures. Insoluble in water; miscible in all proportions with alcohol and ether. *Fuming Sulphuric Acid* does not act upon it; *fuming Nitric Acid* is said to convert amyl into valerianic acid.

Combinations  
of amyl with  
hydrogen.

*Hydroamyl:* AmH=4 volumes gas, is obtained pure when iodide of amyl is decomposed by zinc amalgam in the presence of water; transparent, colorless, extremely mobile fluid, of agreeable, sweet odor. Insoluble in water; easily soluble in alcohol and ether; boils at 31°; sp. gr. 0.6385 at 14°; burns with a clear luminous flame; the strongest reagents show only a slight action upon hydro-amyl.

Amyl and Oxy-  
gen.

*Oxide of Amyl:* AmO=2 volumes gas. This compound should be obtained by the action of an alcoholic solution of potassa upon chloride of amyl in the heat. Agreeably smelling fluid; boils at 111°; other properties are unknown. If we distil amyl spirit with concentrated



sulphuric acid we obtain a mixture of substances, by the distillation of which there goes over, between 175 to 183°, a fluid which is said to consist of  $C_{10}H_{11}O$ ; but this compound cannot, on account of its high boiling point be oxide of amyl. If the oxide of amyl, obtained from chloride of amyl, be completely decomposed by chlorine, and the residue treated with water, this mixture dissolves chloracetic acid,  $(C_4Cl_3)O_3$ . The part insoluble in water, shaken with an alcoholic solution of potassa, leaves a residue which consists of  $(C_4Cl_3)Cl_3$  and  $(C_4Cl_3) \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right.$ ; in the solution is found  $(C_4Cl_3)Cl_3$ , valerianic acid and chloride of potassium.

*Oxyhydrate of Amyl* (amyl-spirit, potato fuselole):  $AmO, HO$ . Crude potato fuselole is a few times distilled over carbonate of soda, then by chloride of calcium deprived of water and afterward rectified; what passes over at 133° is pure amyl-spirit. Completely clear thin-flowing fluid, of peculiar loathsome, suffocating odor, which excites coughing; little soluble in water, miscible, in all proportions, with ether and alcohol. Boiling point 133°; sp. gr. 0.8253. Amyl-spirit behaves to valerianic acid like alcohol to acetic acid, and by the action of oxidizing bodies is converted into that substance. If amyl-spirit be brought together with the air, by means of platinum-black, we thus obtain water and valerianic acid; as mean product, valerianate of amyl is formed. By distillation with *anhydrous phosphoric acid* we obtain amilen, and if the amyl-spirit be conducted through a tube, at dull red heat, it falls into metaceton =  $C_4H_8, \text{ } ^\wedge C_2H = C_6H_6$ .

*Borate of Amyl*:  $AmO, 2BoO_3$ , resembles, in its properties, the borate of ethyl  $AeO, 2BoO_3$ . At 200° it swells up, and can then be drawn into threads; is not decomposed at 300°; burns with green flame; is obtained by the action of anhydrous boracic acid upon amyl-spirit.

Combinations  
of oxide of  
amyl with  
acids.

*Silicate of Amyl*:  $3AmO + SiO_3$ . Colorless, of sharp odor like amyl-spirit; mixes with ether, alcohol, and amyl-spirit, in all proportions; burns with a white flame; boils at 332°; sp. gr. = 0.868.

*Nitrate of Amyl*:  $AmO, NO_3$ , is obtained by introduction of nitrous acid into amyl-spirit. Pale yellow fluid, which becomes darker by warming; sp. gr. = 0.8773; boiling point 91°. *Nitrate of Amyl*:  $AmO, NO_5$ . Amyl-spirit is cautiously distilled with nitric acid, under addition of some urea; boils at 137°; sp. gr. 0.902.

*Sulph-amyl-sulphuric Acid*:  $HO(Am, SO_2)^\wedge SO_3$ , is obtained by the action of dilute nitric acid upon amyl-mercaptan and sulpho-cyanide of amyl. Acid, almost inodorous fluid; gives, with bases, salts soluble in water. The *Baryta Salt* crystallizes in colorless leaflets, unctuous,

Paired combinations of amyl and oxide of amyl.



and soluble in water and alcohol. The *Silver Salt* appears in colorless rhombic tables.

*Amyloxyd-sulphocarbonic Acid*:  $\text{HO}(\text{AmO}, \text{CS}_2) \text{CS}_2$ , is obtained like the corresponding ethyl compound. Colorless or pale yellow fluid, of disagreeable penetrating odor; reddens litmus-paper; is only a little heavier than water, and colors the skin a deep yellow. The *Potassa Salt* appears in white leaflets, soluble in water, alcohol, and ether; if we let *Iodine* act upon the salt, we obtain *Sulphocarbonate of Amyl*  $\text{AmO}, \text{CS}_2$ , a colorless oil, boiling at  $187^\circ$ .

*Amyloxyd-sulphuric Acid*:  $\text{HO}(\text{AmO}, \text{SO}_3) \text{SO}_3$ . Equal parts of amyl-spirit and hydrate of sulphuric acid are mixed together, the mixture after a little time diluted with water, and from the obtained solution the amyloxyd-sulphuric acid is procured in the same manner as the ether-sulphuric acid. Syrup-like, acid mass, easily soluble in water and alcohol. If the aqueous solution be some time boiled, the acid separates into amyl-spirit and sulphuric acid. Gives with bases soluble salts; the *Baryta Salt* forms in shining crystals.

*Protosulphide of Amyl*:  $\text{AmS}$ , an alcoholic solution of  $\text{KS}$  is distilled with chloride of amyl. Highly disagreeable smelling fluid, which boils at  $216^\circ$ . *Bisulphide of Amyl*:  $\text{AmS}_2$ . Yellow, oil-like liquid, of strong odor; boils at  $250^\circ$ ; sp. gr.=0.918.

*Amyl-sulph-hydric Acid* (amyl-mercaptan):  $\text{H}(\text{AmS}) \text{S}$ . We distil an alcoholic solution of  $\text{KS}, \text{HS}$  with  $\text{AmCl}$ . Paired compounds of sulphur and amyl. Oily fluid, of penetrating onion-like odor; strongly refracting light; sp. gr.=0.835; boils at  $117^\circ$ ; behaves towards oxides of metals like the corresponding ethyl compound. The mercury compound  $\text{Hg}(\text{AmS}) \text{S}$  forms a leafy radiant mass, soluble in water, but not easily soluble in ether and alcohol.

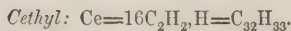
*Iodide of Amyl*: is obtained like iodide of ethyl. Colorless fluid, of biting taste and garlic-like smell; boils at  $146^\circ$ ; sp. gr.=1.5113. Dissolves iodide of mercury abundantly; from the warm solution this separates in the yellow modification.

*Bromide of Amyl*:  $\text{AmBr}$ . Quite resembles iodide of amyl, and is produced in the same manner; heavier than water.

*Chloride of Amyl*:  $\text{AmCl}$ , is obtained by introduction of hydrochloric acid gas into amyl-spirit, and distillation at a gentle heat. Colorless fluid, of rather agreeable aromatic odor; insoluble in water; boils at  $102^\circ$ ; burns with green flame. Gives with *Chlorine*, exposed to sunlight, a colorless fluid, of strong camphor-like odor, and which consists of  $\text{C}_{10}\text{H}_3\text{Cl}_9(3\text{C}_2\text{Cl}_2, \text{C}_2\text{H}_2\text{C}_2\text{H})\text{Cl}_3$ .

*Caproyl*.—If we let the electric current act upon cœnanthylate of potassa we obtain *Caproyl*  $\text{C}_{12}\text{H}_{13}$ , an oily fluid boiling at  $202^\circ$ .

## SIXTEENTH MEMBER.



*Occurrence.*—It is found in spermaceti as oxide of cethyl; unknown by itself.

*Oxyhydrate of Cethyl* (ethal, from eth-er and al-cohol):  $\text{CeO}, \text{HO}$ . Two parts spermaceti (ethalate of cethyl), and one part of hydrate of potassa are united by melting together, and the mass treated first with water, and then with hydrochloric acid. Afterward the whole is warmed, the oily layer which collects upon the surface removed, and repeatedly submitted to the same operation. The mass decomposed by hydrochloric acid is digested with dilute potassa solution in excess, and the ethal of the dried mass is extracted by alcohol. By evaporation of the alcohol, we obtain the ethal, which is purified by distillation. Solid, transparent, wax-like body, inodorous, and tasteless; fuses at  $48^\circ$ , and crystallizes by slow cooling in fine scales. Completely volatile; insoluble in water; miscible with alcohol at  $54^\circ$  in all proportions; sp. gr. = 0.812; boils at  $360^\circ$  (?). By heating with *Hydrate of Potash*, we obtain ethalic acid  $(\text{C}_{32}\text{H}_{31})\text{O}_3$  accompanied by evolution of hydrogen. Repeatedly distilled with *Anhydrous Phosphoric Acid*, ethal decomposes into water and cetin. Potassium, brought into fused ethal, produces a lively evolution of hydrogen.

*Cethyloxyd-sulpho-carbonic Acid*:  $\text{HO}(\text{CeO}, \text{CS}_2)$   $\text{CS}_2$ . A concentrated solution of ethal in sulpho-carbonic acid is mixed with pulverized hydrate of potassa. After a few hours a jelly-like mass is formed from which the potassa salt is extracted by warm alcohol. The salt, which is deposited by cooling as a voluminous powder, consists of  $\text{KO}, (\text{CeO}, \text{CS}_2) \text{CS}_2$ ; hydrochloric acid immediately precipitates pure ethal.

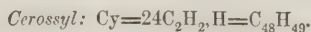
Combination of  
oxyde of ce-  
thyl.

*Cethyloxyd-sulphuric Acid*:  $\text{HO}(\text{CeO}, \text{SO}_3) \text{SO}_3$ . Known only in combination with potassa, in white leaflets of a mother-of-pearl lustre. Is obtained by fusing together ethyl and hydrate of sulphuric acid.

*Chloride of Cethyl*:  $\text{CeCl}$ . Equal volumes of ethal and chloride of phosphorus are heated together in a retort; a lively reaction takes place; at first, the excess of chloride of phosphorus goes over, and at last the chloride of cethyl sublimes. Particularly is not known.

Cethyl and  
chlorine.

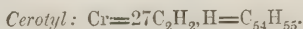
## TWENTY-FOURTH MEMBER.



*Occurrence.*—Upon the surface of the sugar-cane a wax is found, which is named cerosin, and corresponds to the formula  $(\text{C}_{48}\text{H}_{49})\text{O}, \text{HO}$ . This substance seems also to be exuded by other plants;

thus are the gourds gathered in the tropics, covered by a thick layer of this substance. From 36,000 stalks of sugar-cane 72 lbs. cerosin are obtained. The cane is crushed in a mill and the juice expressed. The juice is, without the addition of lime, made to boil by gentle heat and the foam which forms removed. This is dried and in the cold treated with alcohol at  $36^{\circ}$ , which extracts the leaf-wax. The residue is treated with boiling alcohol, the solution strained through thick linen, and the alcohol removed by distillation. White, crystallizable mass, insoluble in cold alcohol, easily soluble in hot; inodorous, burns with beautiful white flame; fuses at  $82^{\circ}$  and crystallizes by slow cooling. Heated with *hydrate of potassa*, it forms cerosinic acid  $\text{HO}(\text{C}_{48}\text{H}_{47})\text{O}_3$  under evolution of hydrogen.

TWENTY-SEVENTH MEMBER.



*Occurrence*.—Is found as oxide of cerotyl in the so-named Chinese wax in combination with cerotinic acid. This wax is generally regarded as vegetable, but it is probably secreted by an insect. At present only the oxide of cerotyl is known.

*Oxyhydrate of Cerotyl* (Cerotin):  $\text{CrO}, \text{HO}$ . Cerotin is procured from Chinese wax, in the same way as ethal from spermaceti. Repeatedly crystallized from alcohol; melts at  $79^{\circ}$ . Heated with hydrate of potassa, it is converted into cerotinic acid  $(\text{C}_{54}\text{H}_{53})\text{O}_3$  under evolution of hydrogen. If *concentrated sulphuric acid* act for several hours in the cold upon finely divided cerotin, we thus obtain *Sulphate of Cerotyl*  $\text{CrO}, \text{SO}_3$ ; the mass is washed with water, then dried in a vacuum, and from the etheric solution the sulphate of cerotyl is obtained in crystals; wax-like mass. If *Chlorine* act upon melted cerotin we obtain a yellowish, transparent, gum-like mass, the chlorcerotinic acid  $=\text{HO}, (6\text{C}_2\text{Cl}_2, 20\text{C}_2\text{H}_2, \text{C}_2\text{H}) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 \end{array} \right. (?)$ . By dry distillation of Chinese wax, a hydro-carbon is formed, which consists of  $\text{C}_{54}\text{H}_{54}$  and melts at  $85^{\circ}$ .

THIRTIETH MEMBER.



*Occurrence*.—Melissyl is found as oxide of melissyl, in combination with palmitinic acid, in beeswax, simultaneously with cerotic acid (cerin). If this wax be boiled with alcohol, the palmitate of melissyl (miricin) remains behind. By melting this with hydrate of potassa we obtain palmitate of potassa and oxyhydrate of melissyl (melissin). If the decomposed mass be treated with boiling alcohol, the melissin separates, during the cooling, as a wax-like mass, which fuses at  $85^{\circ}$ , and heated with hydrate of

potassa is converted into melissic acid  $C_{60}H_{59}O_3$  under evolution of hydrogen. By *Chlorine* it is not easily decomposed; at last is obtained chlormelissic acid  $= (7C_2Cl_2, 22C_2H_2, C_2H) \left\{ \begin{array}{l} O \\ Cl_2 \end{array} \right.$

## SECOND GROUP.

*Formyl Group.*

Component:  $C_2H_2$ ; active molecule: formyl  $= C_2H$ . This is the most numerous group in organic chemistry. At present the following primary members are known.

*Primary Radical: Formyl*  $= C_2H$ .

Member 1.	Acetyl,	Ac =	$C_2H_2, C_2H = C_4H_3$ .
"	2. Propionyl,	Pr =	$2C_2H_2, C_2H = C_6H_5$ .
"	3. Butyryl,	Bu =	$3C_2H_2, C_2H = C_8H_7$ .
"	4. Valeryl,	Va =	$4C_2H_2, C_2H = C_{10}H_9$ .
"	5. Capronyl,	Ca =	$5C_2H_2, C_2H = C_{12}H_{11}$ .
"	6. Oenanthyl,	Oe =	$6C_2H_2, C_2H = C_{14}H_{13}$ .
"	7. Capryl,	Cp =	$7C_2H_2, C_2H = C_{16}H_{15}$ .
"	8. Pelargonyl,	Py =	$8C_2H_2, C_2H = C_{18}H_{17}$ .
"	9. Caprylyl,	Cy =	$9C_2H_2, C_2H = C_{20}H_{19}$ .
"	10. Cocyl,	Co =	$10C_2H_2, C_2H = C_{22}H_{21}$ .
"	11. Laurosteryl,	La =	$11C_2H_2, C_2H = C_{24}H_{23}$ .
"	13. Myristicyl,	My =	$13C_2H_2, C_2H = C_{28}H_{27}$ .
"	14. Benyl,	By =	$14C_2H_2, C_2H = C_{30}H_{29}$ .
"	15. Palmityl,	Pa =	$15C_2H_2, C_2H = C_{32}H_{31}$ .
"	16. Margaryl,	Ma =	$16C_2H_2, C_2H = C_{34}H_{33}$ .
"	17. Stearophanyl,	Sta =	$17C_2H_2, C_2H = C_{36}H_{35}$ .
"	21. Behenyl,	Be =	$21C_2H_2, C_2H = C_{44}H_{43}$ .
"	23. Cerossyl,	Cy =	$23C_2H_2, C_2H = C_{48}H_{47}$ .
"	26. Cerotyl,	Ct =	$26C_2H_2, C_2H = C_{54}H_{53}$ .
"	29. Melissinyl,	Me =	$29C_2H_2, C_2H = C_{60}H_{59}$ .

The radicals of this group all possess the capability of forming acids with 3 atoms oxygen. They also give, at least the lower members of the group, equivalent combinations with sulphur and the halogens. Several of these radicals also unite with 1 atom of oxygen, forming oxides which as hydrates have acquired the general name of *aldehyd*, inasmuch as they can be considered as the corresponding members of the oxyhydrates of the methyl group minus 2 atoms hydrogen; thus is alcohol  $C_4H_5O + HO - 2H =$  Aldehyd  $C_4H_3O + HO$ . Aldehyd reacts indifferently, and possesses the power, by the presence of strong bases, by transposition to change into a resinous mass; they are more volatile than the acids, and by direct oxidation are quickly converted into the acids with 3 atoms oxygen. As the lower members of the oxyhydrates of the methyl group are fluid at ordinary temperatures, but the consistency increases in pro-

A few general chemical relations of this group.

The oxides.  
The aldehyds.

The acids.



portion as the member rises, so likewise are the corresponding members of the acid hydrates fluid at ordinary temperatures; the higher members, on the contrary, appear solid, behave completely like fat, and mostly, as has already been remarked, are found in the fats, and are also generally named fatty acids; indeed, so general a conversion of the fluid acid to the solid takes place, that a limit cannot be fixed. As wood-spirit and alcohol are miscible, in all proportions, with water, so also behave formic, acetic, and propionic acid; but in the degree that  $C_2H_2$  enter, they lose their solubility in water, so that the higher members are completely insoluble; soluble, on the contrary, in alcohol, and particularly in ether. The lower members of the acid hydrates possess a strong acid, penetrating odor, often disagreeable, whilst the higher appear inodorous; the melting point of the latter rises as does the member. All the acids are volatile, and in general each member boils 18 to 20° higher than the foregoing; with the last member that point is so high that it can be volatilized, undecomposed, only in a stream of carbonic acid. Likewise the acids in general are deprived of acid properties as the member rises. Acetic, formic, butyric, propionic, and valerianic acid taste very sour, produce a blister, and leave a white spot upon the tongue, whilst the higher members appear so feebly acid that they scarcely expel carbonic acid. If the higher members be treated with nitric acid, they are by degrees converted into the lower members by oxidation of  $C_2H_2$ ; generally, we obtain a mixture of formic, acetic, butyric, valerianic acid, etc., in different proportions, according to the duration of the action.

Conversion of  
the higher  
members into  
the lower.

Production of  
the derived radicals.

Occurrence and  
formation of  
the primary  
radicals.

By the action of the halogens, particularly chlorine, the primary radicals of this group, by substitution of  $C_2H_2$  by  $C_2Cl_2$ , are converted by degrees into the derived radicals, which combine with O, S, Cl, etc., in the same proportions as the primary. The primary acids are found in nature, but they are also formed by the decomposition of many organic substances, as well as by distillation and fermentation, through oxidizing action. As most of the higher members in combination with oxide of glyceryl present the fats occurring in nature, we obtain the fat acids, by boiling the fats with concentrated alkali solutions, and by decomposition of the obtained salts (soaps), by hydrochloric and sulphuric acid. But since the natural fats are almost always mixtures of several fat-acid combinations, we usually obtain in the way mentioned only mixtures of acids which must then be separated. A few of these acids, as the margaric and stearic are found in nearly all fats of plants and animals whilst others appear only as special fat acids, as cocinic, myristic, laurostearic, etc.

The *Radicals of this Group* correspond, like those of the methyl group, gassiform to 2 volumes.

Formyl gas =  $C_2H$ . Sp. gr. of  $C_2 = 1.6720$

“ “  $H = 0.1386$

Volume of this group as gas ;  
sp. gr. of their  
gases.

$C_2H = 1.8106 = 2$  volumes.

It follows that the sp. gr. of formyl gas = 0.9053

For each addition of  $C_2H_2$  the sp. gr. rises 0.9746

Oxides with O and  $O_3$  are likewise equal 2 volumes.

2 volumes formyl gas = 1.8106

3 “ oxygen = 3.3279

2 “ formic acid gas = 5.1385. Specific gravity = 2.5692.

The oxyhydrates correspond to 4 volumes

2 volumes formic acid = 5.1385

2 “ hydrous gas = 1.2479

4 “ formic acid gas = 6.3864. Sp. gr. = 1.5961.

The *Sulphur Compounds* correspond like the oxygen compounds to 2 volumes gas.

The *Haloid Compounds* with 1, 2, and 3 atoms halogen, are equal 4 volumes gas.

2 volumes formyl gas = 1.8106

6 “ chlorine “ = 14.6400

4 “ chlorformyl “ = 16.4516. Sp. gr. = 4.1126.

The increase of the specific gravity for the introduction of  $C_2H_2$  is above given. The derived radicals and their combinations show the same ratio of atomic volume as the primary.

#### *Primary Radical: Formyl.*

##### a. *Primary Radical* = $C_2H_2 = Fo$ .

*Formyl: Fo.* If the black mass which is often obtained from the heated tartrate of potassa and charcoal in making potassium, be brought into contact with water, a gas is evolved which burns with a clear flame and consists of  $C_2H = 2$  volumes, and can be regarded as formyl.

*Hydrate of Formic Acid:*  $HO, FoO_3$ , is found in ants. Formic acid is produced by oxidation of wood-spirit through the means of platinum-black; by oxidation of alcohol under the co-operation of potassa, by heating the hydrates of oxalic acid, by decomposition of aqueous hydrocyanic acid:  $NC_2H + 3HO = C_2H, O_3 + NH_3$ , by oxidation of turpentine oils, by the action of peroxide of manganese upon tartaric, racemic, and mucic acid, upon sugar, gum, starch—by the action of iodine and hyperiodic acid upon acetic acid, etc. An aqueous solution of formic acid is obtained, if ten parts of tartaric acid with 14 parts peroxide of manganese and 40 parts water be distilled in a capacious retort; or we mix 1 part sugar with 3 parts per-

Compounds of  
formyl with ox-  
ygen.

oxide of manganese, and add little by little 3 parts sulphuric acid previously diluted with 6 parts water; when the evolution of gas ceases, we distil the mixture to dryness. The obtained aqueous solution of formic acid is saturated with carbonate of soda, then evaporated to dryness, and the dry formate of soda distilled with 1 atom hydrate of sulphuric acid, which, however, must be added in very small quantities; an excess of sulphuric acid must be avoided. We obtain the hydrate completely anhydrous, by decomposing the lead salt with hydrosulphuric acid. The hydrate of formic acid appears as a colorless fluid slightly fuming in the air; burns, by heating, with bluish flame, crystallizes at  $0^{\circ}$ , possesses a strongly acid taste, produces a blister; sp. gr. 1.235; boils at  $103^{\circ}$ ; mixes with water

Properties of  
formic acid.

in all proportions. Formic acid suffers no change in the air, but by means of platinum-black decomposes into carbonic acid and water; *Metallic Oxides* which easily yield oxygen, as oxide of mercury, of quicksilver, and the super-oxides completely oxidize the acid even in dilute condition. *Concentrated Sulphuric Acid* decomposes the acid by heat into carbonic oxide and water:  $C_2H_2O_3 = 2CO + HO$ . Bichloride of mercury is converted by formic acid into calomel. The *Formic Acid Salts* are all soluble in water

Formic acid  
salts.

and crystallizable. Drenched with hydrate of sulphuric acid they evolve a suffocating, acid odor like formic acid. Generally formic acid, even in its combinations, can be easily known by its behavior to bichloride of mercury and to the oxides of the precious metals. If it be warmed with a solution of nitrate of silver, metallic silver is immediately precipitated. The *Ammonia Salt* crystallizes in right-angled four-sided prisms; it melts at  $120^{\circ}$  and at  $140^{\circ}$  degrees decomposes into hydrocyanic acid and water. The *Soda Salt*  $NaO, FoO_3 + 2 aq.$  crystallizes in rhombic tables. The *Baryta Salt* dissolves in four parts cold water and is insoluble in alcohol. Also the *Magnesia Salt* is insoluble in alcohol; it crystallizes in fine transparent, anhydrous needles. The *Lead Salt* appears in fine prismatic crystals, soluble in 36 parts cold water and insoluble in alcohol.

*Sulphide of Formyl* (Sulphoform):  $FoS_3$ . We distil 1 part of iodide of formyl with 3 parts finely ground cinnabar. Heavy oil-like fluid, soluble in alcohol and ether, of sweet aromatic odor. Gives with pure potassa formate of potassa and sulphide of potassium.

Formyl and sul-  
phur.

*Iodide of Formyl* (Iodiform):  $FoI_3$ , is obtained by the action of iodine upon an alcoholic solution of potassa. To a mixture of equal parts carbonate of potassa and alcohol with 3 parts of water, iodine is added, so long as the color vanishes and the produced iodide of formyl precipitated by diluting with water. From the alcoholic solution iodide of formyl forms large, yellow crystals of mother-of-pearl lustre and easily

Iodine and ha-  
logen.

pulverized; it possesses a strong saffron-like odor and a sweetish, disagreeable taste; fuses at  $100^{\circ}$ , sublimes at a lower temperature and decomposes, in powerful heat, into iodine, iodide of hydrogen and carbon. Gives, with an alcoholic solution of potassa, formate of potassa and iodide of potassium.

*Bromide of Formyl* (Bromoform):  $\text{FoBr}_3$ . Dilute wood-spirit, alcohol or aceton is distilled with a dilute solution of bromide of lime. A water-clear etheric-smelling fluid of a penetrating sweet taste, insoluble in water, miscible with alcohol and ether in all proportions; heavier than water.

*Chloride of Formyl*:  $\text{FoCl}$ . To an alcohol solution of potassa the so-named chloride of paraacetyl,  $(\text{C}_2\text{HCl}, \text{C}_2\text{H}_2)\text{Cl}_2$  (V. Elayl), is added; much chloride of potassium is precipitated, whilst by distillation of this mixture a colorless fluid chloride of formyl goes over; the same combination also appears to be formed by the action of aqueous potassa upon the chloracetate of methyl  $(\text{MeO}, \text{C}_4\text{Cl}), \text{O}_3$ . Oily, insoluble in water, miscible in all proportions with alcohol and ether.

*Bichloride of Formyl*:  $\text{FoCl}_2$ . Chloride of formyl combines directly with chlorine, forming  $\text{FoCl}_2$  also  $\text{FoCl}_3$  and  $(\text{C}_2\text{Cl})\text{Cl}_3$ .

*Terchloride of Formyl* (Chloroform):  $\text{FoCl}_3$ . We distil a mixture of 3 parts water,  $\frac{1}{4}$  part alcohol, and 1 part of chloride of lime, or a mixture of equal parts of acetate of lime and chloride of lime with 5 to 6 parts water. In both cases terchloride of formyl is precipitated by water from the distillate, then washed several times with water and rectified over chloride of calcium. (If we employ wood-spirit instead of alcohol we obtain terchloride of formyl, also some empyreumatic oil.) Water-clear, thin-flowing, sweet liquid of penetrating odor. Specific gravity 1.480; boiling point  $60^{\circ}$ ; becomes solid by rapid evaporation. Inhaled it completely stupefies all the senses. Insoluble in water, mixes with alcohol and ether in all proportions. By heating falls into  $\text{C}_2\text{Cl}, \text{HCl}$  and  $\text{Cl}$ , and by conduction through a glowing porcelain tube separates into terchloride of chloracetyl  $(\text{C}_4\text{Cl}_3)\text{Cl}_3$ , hydrochloric acid and carbon,  $3(\text{C}_2\text{H})\text{Cl}_3 = (\text{C}_4\text{Cl}_3)\text{Cl}_3 + 3\text{HCl} + \text{C}_2$ . By the action of chlorine is converted slowly into  $(\text{C}_2\text{Cl})\text{Cl}_3$  and gives, brought together with an alcoholic solution of potassa, formate of potassa and chloride of potassium.

*Oxychloride of Formyl*:  $\text{Fo} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ , is obtained by the action of chlorine upon oxide of methyl. At first is produced  $\text{MeO}, \text{Fo} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$  and later  $\text{Fo} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ . Easily movable fluid, of suffocating, tear-exciting odor; exhales acid vapors into the air, and by the influence of chlorine under the operation of light is converted into  $(\text{C}_2\text{Cl}) \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ .



*Sulphochloride of Formyl*:  $\text{Fo} \left\{ \begin{smallmatrix} \text{S} \\ \text{Cl}_2 \end{smallmatrix} \right.$ . If we let chlorine act upon simple sulphide of methyl, we first obtain the above fluid sulphochloride of formyl, and later  $(\text{C}_2\text{Cl}) \left\{ \begin{smallmatrix} \text{S} \\ \text{Cl}_2 \end{smallmatrix} \right.$ .

*Iodochloride of Formyl*:  $\text{Fo} \left\{ \begin{smallmatrix} \text{I} \\ \text{Cl}_2 \end{smallmatrix} \right.$ . We distil iodide of formyl with solid chloride of phosphorus. A yellow fluid: sp. gr. 1.69; by concentrated aqueous solution of potassa, is separated into formic acid, chloride of potassium, and iodide of potassium.

*Bromiodide of Formyl*:  $\text{Fo} \left\{ \begin{smallmatrix} \text{Br} \\ \text{I}_2 \end{smallmatrix} \right.$ . Bromine brought together with iodide of formyl produces iodide of bromine and bromiodide of formyl; the former is absorbed by shaking with potassa solution. Oily, yellow fluid.

*Formate of Oxychloride of Formyl*:  $\text{Fo} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right., \text{FoO}_3$ . Arises by the action of chlorine upon the formate of methyl. Water-clear fluid.

*Formyl-sulphochloride-sulphuric Acid*:  $\text{HO, Fo} \left\{ \begin{smallmatrix} \text{SO}_2 \\ \text{Cl}_2 \end{smallmatrix} \right., \text{SO}_3$ . We treat sulphite of chloride of Chlorformyl  $(\text{C}_2\text{Cl})\text{Cl}, 2\text{S O}_2$  with a solution of potassa:  $(\text{C}_2\text{Cl})\text{Cl}, 2\text{SO}_2 + 2\text{HO} = \text{HO}(\text{C}_2\text{H}) \left\{ \begin{smallmatrix} \text{Cl}_2 \\ \text{SO}_2 \end{smallmatrix} \right., \text{SO}_3$ , or we dissolve metallic zinc in chlorformyl-sulpho-chlor-sulphuric acid, precipitate the oxide of zinc from the solution by carbonate of potassa, filter, evaporate and extract the dry residue with boiling alcohol. After cooling, the potassa salt separates from the alcoholic solution. From the alcoholic solution of potassa salt we separate the potassa by sulphuric acid; filter, and leave the acid to crystallize. Colorless, small columns of very sour taste, deliquescent, decomposes at higher temperatures, and with bases gives soluble salts.

#### b. Derived Radical. Chlorformyl = $\text{C}_2\text{Cl}$ .

*Chlorformyl*:  $\text{C}_2\text{Cl}$ , is produced by repeated sublimation of chloride of formyl. White, tasteless, inodorous needles, of silken lustre, insoluble in water, easily soluble in alcohol, fusible and sublimable; decomposes at higher temperatures into chlorine and carbon.

*Chlorformic Acid*:  $(\text{C}_2\text{Cl})\text{O}_3$ , arises by the action of wood-spirit or alcohol upon oxychloride of chlorformyl under the production of chlorformate of methyl or of ethyl  $2(\text{C}_2\text{Cl}) \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right. + 2\text{MeO}, \text{HO} = 2(\text{MeO}, (\text{C}_2\text{Cl})\text{O}_3) + 2\text{HCl}$ . Unknown in an isolated condition.

*Chloride of Chlorformyl*:  $(\text{C}_2\text{Cl})\text{Cl}_3$ . It is produced by the com-

plete decomposition of chloride of methyl by chlorine, likewise by the action of chlorine upon chloride and bichloride of formyl; colorless liquid of strong aromatic odor; sp. gr. 1.599; boils at  $78^{\circ}$ ; by conduction through a glowing tube, separates into *bichloride of chlorformyl*  $(C_2Cl)Cl_2$ , and *chloride of chlorformyl*,  $(C_2Cl)Cl$ . This last combination is also obtained if chloride of chloracetyl  $(C_4Cl_3)Cl$  be repeatedly conducted through a glowing tube. Crystallizes from the etheric solution in fine white tasteless needles of fat-like odor, which sublime at  $150$  to  $200^{\circ}$ . At higher temperatures the compound decomposes into chlorine and carbon.

*Oxychloride of Chlorformyl*:  $(C_2Cl)\left\{\begin{smallmatrix} O \\ Cl_2 \end{smallmatrix}\right.$ , arises by the complete decomposition of oxide of methyl by chlorine, like the oxychloride of formyl. Fluid. Sp. gr. 1.594; boiling point  $100^{\circ}$ , of suffocating odor.  $(AeO)$  boils at  $35^{\circ}$  and  $AeCl$  at  $12^{\circ}$ ;  $(C_2Cl)Cl_3$  boils at  $78^{\circ}$  and  $(C_2Cl)\left\{\begin{smallmatrix} O \\ Cl_2 \end{smallmatrix}\right.$  at  $100^{\circ}$ ; therefore, in both cases, the substitution of  $Cl$  by  $O$  produces an elevation of  $23$  to  $24^{\circ}$ .)

*Sulphochloride of Chlorformyl*:  $(C_2Cl)\left\{\begin{smallmatrix} S \\ Cl_2 \end{smallmatrix}\right.$ , is obtained by the action of chlorine upon sulphochloride of formyl; fluid.

*Chlorosulphide of Chlorformyl*:  $(C_2Cl)\left\{\begin{smallmatrix} Cl \\ S_2 \end{smallmatrix}\right.$  (?). If terchloride of chlorformyl gas and hydrosulphuric acid be conducted together through a moderately heated tube, or if we distil sulpho-carbonic acid with hydrochloric acid and peroxide of manganese, we obtain a yellow oil of an odor which powerfully irritates the eyes; sp. gr. 1.46; boiling point  $70^{\circ}$ . Left standing a long time with potash lye the compound separates into  $(C_2Cl)Cl_3 + 2CO_2$  under the production of  $4KS$ .

*Chlorformate of Oxychloride of Chlorformyl*:  $(C_2Cl)\left\{\begin{smallmatrix} O \\ Cl_2 \end{smallmatrix}\right. + (C_2Cl)O_3$ , is obtained by the complete decomposition of formate of methyl by chlorine. Water-clear, very thin fluid of 0.724 sp. gr. boils at  $180^{\circ}$ ; of suffocating odor.

*Sulphite of Chloride of Chlorformyl*:  $(C_2Cl)Cl \cdot 2SO_2$ . If sulphurous acid be conducted into an alcoholic solution of sulphite of terchloride of chlorformyl, we obtain sulphite of chloride of chlorformyl under the production of sulphuric and hydrochloric acid. It is known only in solution; it is colorless and inodorous, is again converted into sulphite of terchloride of chlorformyl by the introduction of chlorine; by treatment with solution of potassa we obtain the sulphide of sulpho-chloride of chlorformyl  $(C_2Cl)\left\{\begin{smallmatrix} Cl_2 \\ SO_2 \end{smallmatrix}\right. \cdot SO_3$ .

*Sulphite of Terchloride of Chlorformyl* (Berzelius and Mercet's combination):  $(C_2Cl)Cl_3 \cdot 2SO_2$ . A bottle holding six quarts, is

Paired combinations of chlorformyl.

half filled with concentrated hydrochloric acid, then a quantity of peroxide of manganese sufficient for preparing chlorine, and afterwards 50 grains of sulpho-carbonic acid are added. The closed bottle is at first preserved in a cool place and then exposed a few days to a temperature of  $30^{\circ}$ , accompanied by often removing the stopper, or also set in the sunlight, and afterward distilled; in the beginning, chlorine and sulpho-carbonic acid are evolved, and at last the combination is sublimed. Water-clear rhombic tables of a velvet lustre, and which fuse at  $135^{\circ}$ , and boil at  $170^{\circ}$ . The vapor possesses a penetrating tear-exciting odor, and causes, when inspired in large quantity, an extremely violent itching in the œsophagus. By heating with potassa or baryta is converted into the following compound.

*Chlorformyl sulphochlorid-sulphuric Acid:*  $\text{HO}(\text{C}_2\text{Cl}) \left\{ \begin{array}{l} \text{SO}_2 \\ \text{Cl}_2 \end{array} \right. \text{S}$   
 $\text{O}_3$ . From the aqueous solution of the baryta salt of this acid, which is obtained by the action of baryta upon the above compound, the baryta is precipitated by sulphuric acid; after evaporation, we obtain the acid in colorless small columns which fuse at  $130^{\circ}$ , and volatilize at  $160^{\circ}$ , partly undecomposed, and in the air deliquesce. Metallic zinc dissolves in the acid without evolution of gas, under the production of formyl-sulpho-chlorid-sulphuric acid. If the potassa salt dissolved in water be exposed to the galvanic current we obtain sulpho-methyl-sulphuric acid  $(\text{Me}, \text{SO}_2) \text{SO}_3$ . If we bring together the hydrous acid, and an amalgam of one part potassium to 100 parts quicksilver, formyl sulpho-chloride sulphuric acid is produced, and by a larger quantity of amalgam we obtain at last sulpho-methyl-sulphuric acid, and as mean member the so-named chlor-elayl-hyposulphuric acid  $\text{Fo} \left\{ \begin{array}{l} \text{SO}_2 \\ \text{Cl}_2 \end{array} \right. \text{SO}_3 + ^-(\text{Me}, \text{SO}_2) \text{SO}_3 =$   
 $\text{C}_2\text{H}_2, \text{ClS}_2\text{O}_5$ . A strongly acid fluid of syrup-thickness at  $-16^{\circ}$ , which, however, suffers no decomposition at  $140^{\circ}$ , and with bases forms salts mostly crystallizable, and soluble in water.

PAIRED RADICALS, CONSISTING OF THE RADICALS OF THE METHYL GROUP AND FORMYL.—THE ELAYL GROUP.

By the combination of formyl with the different members of the methyl group and with hydrogen, paired double radicals arise, which correspond in gaseous form to 4 volumes. They arise from the radicals of the methyl group; thus, by distillation of oxide of methyl with sulphuric acid, we obtain methylen= $\text{H}, ^-\text{Fo}$ ; in the same manner from oxide of ethyl is obtained elayl  $\text{Me}, ^-\text{Fo}$ , etc. The oxygen withdraws, accordingly, one atom H from the component  $\text{C}_2\text{H}_2$  and thereby arises formyl, which remains paired with  $\text{H}, \text{C}_2\text{H}_3, \text{C}_4\text{H}_5$ , etc. Whilst, therefore, methyl  $\text{C}_2\text{H}_2$  with H forms a common whole= $2$  volumes gas, elayl, e. g. is a paired compound of two independent radicals, methyl with formyl, and corresponds



therefore to 4 volumes gas. From ethyl  $C_2H_5, C_2H_5, H$  is formed, therefore,  $C_2H + C_2H_5, H$ . The radicals of the elayl group arise also by the dry distillation of the acids of the formyl group, especially the higher members of the same, also by the dry distillation of most organic acids; they all possess the capability of uniting directly with two atoms chlorine or bromine, forming oil-like combinations, in which respect they differ from other hydrocarbons. Thus arises chloreelayl from  $(C_2H_3, ^\wedge C_2H)Cl_2 = (Me, ^\wedge Fo)Cl_2$ , or it exhibits a paired combination of chloride of methyl with chloride of formyl  $= MeCl, ^\wedge FoCl$ .

*Methylen* (Hydroformyl):  $H, ^\wedge C_2H = C_2H_2$ . Colorless gas, burning with a clear flame; combines with chlorine under the co-operation of sunlight. Is obtained if chloromethyl be conducted through a glowing porcelain tube; the hydrochloric acid simultaneously produced is absorbed by shaking with water.

1st Member.  
Methylen,  $H, ^\wedge$   
Fo.

*Elayl* (Methyl-Formyl; Olefiant Gas):  $C_2H_3, ^\wedge C_2H = C_4H_4$ , is produced by dry distillation of organic compounds possessing little oxygen. We obtain it in the simplest manner, by heating one part alcohol of 0.83 sp. gr. with 3 to 4 parts hydrate of sulphuric acid. The gas which escapes is conducted through milk of lime, to remove the carbonic and sulphurous acid, and then left some time standing over water to remove the etheric and alcoholic vapor. Colorless gas of disagreeable suffocating odor, slightly soluble in water, alcohol, and ether; sp. gr. of its vapor  $= 0.969$ . If, by means of a pump, the gas be pressed into a condensation vessel, cooled in a vacuum to  $-110^\circ$  by a mixture of ether and solid carbonic acid, a water-clear fluid is produced; elayl gas burns with a clear luminous flame, and by being conducted through a glowing tube separates into  $C_2$  and hydromethyl  $(C_2H_3)H$ . If the gas be quickly mixed with two volumes of chlorine gas, and the mixture immediately inflamed, carbon is precipitated in the form of soot, under the production of hydrochloric acid.

2d Member.  
Elayl,  $Me, ^\wedge Fo$ .

*Bisulphide of Elayl*:  $(C_2H_3, C_2H)S_2 = C_2H_3, S + ^\wedge C_2H, S = C_4H_4, S_2$ . An alcoholic solution of sulphide of potassium is saturated with chloride of elayl. After some days the fluid assumes a clear red color, accompanied by the production of  $K_2(C_4H_4, S_2)S_2$ . If air acts upon the solution, there is precipitated an extremely loose crystalline white powder, of sweetish taste and smell. Insoluble in water, non-volatile, not easily soluble in alcohol, is not attacked by even boiling potash lye.

Compounds of  
elayl.

*Tetrasulphide of Elayl*:  $(C_2H_3, C_2H)S_4 = C_2H_3, S + ^\wedge C_2H, S_3 = C_4H_4, S_4$ . It is obtained like the former compound, by the employment of bisulphide of potassium and agrees with that substance in its properties. Chlorine and bromine decompose both compounds.



An alcoholic solution of quinquiesulphide of potassium, brought together with chloride of elayl, gives a yellow, tenacious, elastic mass, insoluble in potash lye, and which contains 10 atoms sulphur.

*Elayl-hydrosulphuric Acid:*  $H_2(C_2H_3, ^-C_2HS_2)^-S_2=C_4H_6S_4$ . If the alcoholic solution of  $KS, HS$  be distilled with chloride of elayl, a fluid goes over which possesses the most disagreeable mercaptan odor, and is a solution of elayl-hydrosulphuric acid. This solution, diluted with water, gives a green precipitate with salts of peroxide of iron, a blue with salts of copper, and a yellow with salts of lead; the last consists of  $Pb_2(C_4H_4S_2)_2S_2$ . If the alcoholic solution be left standing a long time in the air, a white flocculent precipitate is obtained, which appears to consist of tetrasulphide of elayl and elayl-hydrosulphuric acid.

*Sulphelayl-sulphuric Acid.* If we let nitric acid operate upon tetrasulph-elayl, we obtain sulphuric acid and sulphelayl-sulphuric acid  $= 2HO(C_2H_3, ^-SO_2, SO_3 + C_2H, ^-SO_2)^-2SO_3$  (?) The baryta salt soluble in water, contains 2 atoms baryta; by saturating the baryta through the means of sulphuric acid we obtain the pure acid, which crystallizes in small white acid-tasting crystals.

*Iodide of Elayl:*  $(C_2H_3, C_2H)I_2=C_2H_3I + ^-C_2HI$ . It is directly obtained by bringing together iodine and elayl gas in a gentle heat. Crystallizes from the alcoholic solution in long flexible white needles of penetrating, tear-exciting odor; insoluble in warm water, easily soluble in alcohol and in ether; decomposes at  $85^\circ$  under separation of iodine. Chlorine and bromine separate iodine by the production of chloride or bromide of elayl. Treated with an alcoholic potassa solution, gives protiodide of methylen-formyl  $(H, ^-C_2H + C_2H)I=C_4H_3I$ .

*Bromide of Elayl:*  $(C_2H_3, C_2H)Br_2=C_2H_3Br + ^-C_2HBr$ , is directly obtained by shaking bromine with elayl gas. Thin-flowing, etheric-smelling, colorless fluid, of penetrating sweet taste; crystallizes at  $0^\circ$ ; sp. gr. 2.164; boiling point  $129.5^\circ$ . Treated with an alcoholic solution of potassa it gives protobromide of methylen-formyl  $(H, C_2H + C_2H)Br$ .

*Chloride of Elayl:*  $(C_2H_3, C_2H)Cl_2=C_2H_3Cl + ^-C_2HCl$ . It is produced if pure moist elayl gas and chlorine gas are conducted in common into a cooled balloon, or if we slowly conduct elayl gas over superchloride of antimony. The obtained oily fluid is several times distilled with sulphuric acid and potassa solution. Colorless fluid, of agreeable etheric odor and sweet aromatic taste, in water a little, but in alcohol and ether easily soluble. Sp. gr. 1.25; boiling point  $82.4^\circ$ ; burns with green, strongly sooty flame; by conduction through a glowing tube decomposes into hydrochloric acid, carbon hydromethyl, and elayl. If the chloride of elayl be warmed with an alcoholic solution of potassa, protochloride of methylen-formyl escapes  $(H, ^-C_2H + ^-C_2H)Cl$  accompanied by the produc-

tion of chloride of potassium. The same appears as a colorless gas, easily soluble in alcohol and ether, and is fluid at  $-18^{\circ}$ , possesses a garlic-like odor, and burns with a green flame. This compound combines directly with chlorine in the sunlight, forming terchloride of methylen-formyl  $(\text{H}\text{---}\text{C}_2\text{H}\text{---}\text{C}_2\text{H})\text{Cl}_3$ . This last is an agreeable-smelling fluid, which boils at  $115^{\circ}$ , and possesses a sp. gr. = 1.422; if it be brought together with an alcoholic solution of potassa, chloride of potassium, water, and chloride of formyl  $(\text{C}_2\text{H})\text{Cl}$  are produced. If we let chlorine act upon the chloride of elayl, there is obtained a combination of bichlorides of chlorformyl and of formyl  $= (\text{C}_2\text{Cl})\text{Cl}_2 + \text{---}(\text{C}_2\text{H})\text{Cl}_2 = \text{C}_4\text{HCl}_4$ . A honey-like smelling fluid, of sweet and burning taste; boils at  $153^{\circ}$ ; sp. gr. 1.662. With an alcoholic solution of potassa, gives a combination of chlorformyl with bichloride of chlorformyl  $= \text{C}_2\text{Cl}\text{---}(\text{C}_2\text{Cl})\text{Cl}_2 = \text{C}_4\text{Cl}_4 = (\text{C}_4\text{Cl}_3)\text{Cl}$ ; with chlorine, exposed to sunlight, we obtain terchloride of chloracetyl  $(\text{C}_4\text{Cl}_3)\text{Cl}_3$ .

*Oxychloride of Elayl*:  $(\text{C}_2\text{H}_3\text{---}\text{C}_2\text{H}) \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix} \right.$  is produced simultaneously with chloride of elayl, if elayl and chlorine in moist condition operate on each other. If the raw product be distilled, chloride of elayl goes over at  $180^{\circ}$ . Water-clear, colorless fluid, of sweetish etheric smell; burns with green flame; is decomposed by water, alkalies, and sulphuric acid, accompanied by evolution of chloride of elayl.

*Elayl-platinum*. If chloride, or sulphate of platinum, be heated with alcohol, a heavy flocculent powder is precipitated, which consists of elayl and platinum. It possesses, in a remarkable degree, the capability of absorbing gas, particularly oxygen.

*Sulphate of Elayl*:  $(\text{C}_2\text{H}_3\text{---}\text{C}_2\text{H})2\text{SO}_3 = \text{C}_2\text{H}_3\text{---}\text{SO}_3\text{---} + \text{C}_2\text{H}\text{---}\text{SO}_3$ , is obtained if completely dry elayl gas and anhydrous sulphuric acid are brought into contact with each other; it forms a white crystalline mass, which melts at  $80^{\circ}$ , and after cooling stiffens crystalline. If the compound be brought in contact with water we obtain a paired acid, the isäthionic, which consists of  $\text{HO}(\text{H}\text{---}\text{C}_2\text{H}\text{---} + \text{---}\text{C}_2\text{H}_3\text{O}\text{---}\text{SO}_3)\text{---}\text{SO}_3$  or of sulphate of <sup>Isäthionic acid.</sup> methylen-methyloxyd, paired with sulphuric acid, and is metamerie with ether sulphuric acid. Isäthionic acid is also obtained by the decomposition of sulphate of ethyl, by water. It possesses a strong acid taste, and is not decomposed by boiling with water; with bases it produces salts, easily soluble in water, but with difficulty in alcohol; if it be heated with hydrate of potassa it is, without blackening, decomposed, accompanied with evolution of hydrogen gas; as residue remains a mixture of sulphurous and sulphuric acid salts.

*Elayl-sulphuric Acid (Sulphate of Carbyl)*:  $(\text{C}_2\text{H}_3\text{---}\text{C}_2\text{H})4\text{SO}_3 = (\text{C}_2\text{H}_3\text{---}\text{SO}_3 + \text{---}\text{C}_2\text{H}\text{---}\text{SO}_3)\text{---}2\text{SO}_3$ . We place a glass tube, filled with absolute alcohol, in a bottle containing anhydrous sulphuric acid. After some time crystals are produced, which melt by cautious

heating, and after cooling stiffen to a crystalline mass; exposed to the air it absorbs water under the production of ethionic acid, a paired acid, which contains isäthionic acid as pairing combined with 2 atoms sulphuric acid. This acid saturates 2 atoms of base; by warming the aqueous solution it decomposes into isäthionic and sulphuric acid.

*Ether-sulphate of Elayl* (Heavy Oil of Wine):  $2\text{AeO}, \text{SO}_3 + (\text{C}_2\text{H}_3, \text{SO}_3 + \text{C}_2\text{H}, \text{SO}_3)$ , v. ether-sulphuric acid.

*Propylen* (ethyl-formyl):  $\text{C}_4\text{H}_5, \text{C}_2\text{H} = \text{C}_6\text{H}_6$ . This compound is produced when amyl-spirit is conducted through a redhot glass tube, as well as by the dry distillation of the higher members of the acids of the formyl series; it appears also to be produced in the electrification of a concentrated solution of butyrate of potassa. Pure propylen gas has not yet been produced; that which is obtained by decomposition of amyl-spirit appears to contain one-half marsh gas.

*Bromide of Propylen*:  $(\text{C}_4\text{H}_5, \text{C}_2\text{H})\text{Br}_2 = \text{C}_4\text{H}_5, \text{Br} + \text{C}_2\text{H}, \text{Br}$ . Bromine is added in drops to a gaseous mixture, which contains propylen, so long as the color vanishes. A fluid product is obtained, which is washed with water, then dried over chloride of calcium, and purified by repeated rectification over quicklime. Colorless, etheric fluid, of sharp garlic-like odor, insoluble in water, miscible with alcohol and ether in every proportion; boils at  $143^\circ$ ; sp. gr. 1.7; weight of the vapor = 7.31. Treated with an alcoholic solution of potassa it produces bromide of potassium and  $(\text{H}, \text{C}_4\text{H}_3, \text{C}_2\text{H})\text{Br} = \text{Bromide of hydroacetyl-formyl}$ ; a colorless, heavy, mobile liquid, smelling like putrid fish; boils at  $45^\circ$ ; gives, with 2 atoms bromine,  $(\text{H}, \text{C}_4\text{H}_3, \text{C}_2\text{H})\text{Br}_3$ . If this compound be treated with an alcoholic solution of potassa, we obtain bromide of acetyl-formyl  $= (\text{C}_4\text{H}_3, \text{C}_2\text{H})\text{Br}_2$ ; besides this there still exist compounds which correspond to the formulæ  $(\text{C}_4\text{H}_3, \text{Br}, \text{C}_2\text{H})\text{Br}_3 = \text{C}_6\text{H}_4\text{Br}_4$ ;  $(\text{C}_4\text{H}_3, \text{Br}, \text{C}_2\text{Br})\text{Br}_3 = \text{C}_6\text{H}_3\text{Br}_5$  and  $\text{C}_4\text{H}_3, \text{C}_2\text{Br} = \text{C}_6\text{H}_3\text{Br}$ .

*Chloride of Propylen*:  $(\text{C}_4\text{H}_5, \text{C}_2\text{H})\text{Cl}_2 = \text{C}_4\text{H}_5, \text{Cl} + \text{C}_2\text{H}, \text{Cl}$ . It is obtained by the action of chlorine gas upon propylen gas. Etheric-smelling fluid, of 1.151 sp. gr.; boils at  $104^\circ$ . Gives, by repeated treatment with an alcoholic solution of potassa and chlorine, gradually, the following combinations:  $(\text{H}, \text{C}_4\text{H}_3, \text{C}_2\text{H})\text{Cl}_3$ ;  $(\text{C}_4\text{H}_3, \text{Cl}, \text{C}_2\text{H})\text{Cl}_3$ ;  $(\text{C}_4\text{H}_3, \text{Cl}, \text{C}_2\text{Cl})\text{Cl}_3$ ;  $(\text{C}_4\text{Cl}_3, \text{Cl}, \text{C}_2\text{H})\text{Cl}_3 = \text{C}_6\text{HCl}_7$  and  $(\text{C}_4\text{Cl}_3, \text{Cl}, \text{C}_2\text{Cl})\text{Cl}_3 = \text{C}_6\text{Cl}_8$ .

*Valylen* (Butyren):  $\text{C}_6\text{H}_7, \text{C}_2\text{H} = \text{C}_8\text{H}_8$ . If, by an electric current, we decompose a concentrated aqueous solution of valerianate of potassa, and conduct the evolved gas through refrigerated alcohol, then through water, and at last over hydrate of potassa, there remains a mixture of hydrogen gas and valylen gas, which last can be absorbed by chlorine. It is also produced when fat is conducted through a tube at gentle red heat. If the obtained gas be strongly com-

3d Member.  
Propylen, Ae  
Fo.

4th Member.  
Valylen, Pr  
Fo.



pressed, a thin mobile oil separates, which is a mixture of valylen with other hydrocarbons. If this mixture be distilled at from  $-18^{\circ}$  to  $0^{\circ}$ , valylen goes over and can be collected as a gas. It exhibits, at  $18^{\circ}$ , a water-clear liquid of 0.627 sp. gr.; boils at  $0^{\circ}$ . Water takes up only a little of it; by alcohol and ether it is in greater part absorbed. Sulphuric acid absorbs 100 volumes of valylen gas, producing a paired acid.

*Bichloride of Valylen*:  $(C_6H_7, \wedge C_2H)Cl_2$ . Chlorine gas combines with valylen, forming a colorless, clear, etheric fluid, of a sweetish aromatic taste; by the farther action of chlorine in the sunlight there remains at last a tough mass. The chloride of valylen boils at  $123^{\circ}$ ; sp. gr. 1.112.

*Amylen* (Valeren):  $C_8H_9, \wedge C_2H = C_{10}H_{10}$ , is produced by distillation of amyl-spirit with anhydrous phosphoric acid, or with chloride of zinc, simultaneously with paramylen  $C_{20}H_{20}$ , and metamylen  $C_{40}H_{40}$ . It is also formed, beside amyl, by decomposition of the iodides of amyl by zinc, at a high temperature. Colorless, clear liquid, of peculiar disagreeable odor; boils at  $36^{\circ}$ ; is completely absorbed by superchloride of antimony and fuming sulphuric acid. It combines with 2 atoms of chlorine and bromine.

*Oleen* (Amyl-formyl):  $C_{10}H_{11}, \wedge C_2H = C_{12}H_{12}$ . By the distillation of hydro-oleinic acid, an oily fluid goes over; if the same be repeatedly submitted to fractional distillation, the oleen goes over at  $55^{\circ}$  and the elaen at  $100^{\circ}$ .

The oleen is a colorless, garlic-like smelling fluid, insoluble in water, and easily soluble in alcohol and ether; burns with a clear flame, and produces, with chlorine, a liquid etheric compound which contains 2 atoms chlorine; it unites also with 2 atoms bromine. Olaen appears also to produce, by dry distillation, doeglinic acid.

*Elaen*:  $C_{14}H_{15}, \wedge C_2H = C_{16}H_{16}$ , resembles oleen, and combines, like it, with 2 atoms chlorine and bromine.

To this series belong, yet farther, *paramylen*  $C_{20}H_{20}$ , *ceten*  $C_{32}H_{32}$ , *metamylen*  $C_{40}H_{40}$ , *ceroten*  $C_{54}H_{54}$ , and *melen*  $C_{60}H_{60}$ . (We compare ethal, cerotyl, and melyssyl.) Moreover, gaseous mixtures arise by dry distillation of organic combinations containing little oxygen; of these a part is absorbed by chlorine. The constitution of these substances is not yet known. Here belongs also the so-called *eupion*.

Hydrocarbons which do not combine with chlorine, but also consist of *equal atoms of carbon and hydrogen*, are, e. g., *Hatschetin*, a transparent fossil-substance of wax consistence, occurring at Glamorganshire in England, consists, apparently, of  $C_{16}H_{16}$ ; *Ozokerite* (fossil-wax) is found in Moldau, near Slamik, in masses of 10 to 100 lbs.; burns with beautiful, slightly sooty flame; melts at  $62^{\circ}$ ; *Paraffin*, a product of dry distillation, completely white,



shining, crystalline, burns with beautiful luminous flame, completely indifferent, etc.

#### FIRST MEMBER.

*Acetyl*: Primary Radical,  $\text{Ac} = (\text{C}_2\text{H}_2, \text{C}_2\text{H}) = \text{C}_4\text{H}_3$ .

*Occurrence and Production*.—Acetyl is found combined with oxygen as acetic acid, sometimes free, and sometimes combined with the sap of many trees. Like formyl, it is produced in many ways, as from ethyl and its combinations through affinity for  $\text{H}_3$ , sometimes by the oxygen of the air under the co-operation of platinum, or ferment, sometimes by the operation of oxidizing substances, as chloric acid, etc. (s. ether and alcohol); further by the spontaneous decomposition of many organic compounds, even when air is excluded (in this way tartaric and citric acid in watery solution, are converted into acetic acid) by the dry distillation of most non-volatile, non-nitrogenous compounds, as wood, gum, starch, by the action of peroxide of manganese and other superoxides upon many organic substances, and likewise by the influence of hydrate of potash in high temperatures upon tartaric, citric, saccharic, mucic acid, etc., by heating several organic substances with hydrated sulphuric acid, etc.

*Oxyhydrate of Acetyl* (Aldehyd):  $\text{HOAcO}$ . A mixture of 4 parts alcohol of 80 per cent., 6 parts peroxide of manganese, 6 parts sulphuric acid, and 4 parts water are submitted to distillation at a gentle heat, and on account of the volatility of aldehyd, the receiver is strongly refrigerated; the distillation is interrupted if the distillate has an acid reaction. The distillate is repeatedly rectified over chloride of calcium, and then is exhibited a mixture of aldehyd, acetal, ether, acetate of ethyl, and alcohol.

The same is mixed with two parts ether and saturated with ammonia; crystals are produced of  $\text{NH}_4\text{O}, \text{AcO}$ , which are insoluble in ether. The same is dissolved in an equal quantity of water and distilled with a mixture of three parts sulphuric acid, and four parts water. The aldehyd escaping accompanied by lively effervescence is condensed by a good cooling apparatus, and its water removed by chloride of calcium. A colorless, easily-flowing fluid, of peculiar, ether-like, suffocating odor; inhaled, produces cramp of the breast. Aldehyd mixes with water, alcohol, and ether, in all proportions, accompanied by elevation of temperature; chloride of calcium separates it from the watery solution, shows no acid reaction, dissolves iodine, sulphur, and phosphorus, is very inflammable, boils at  $21.^\circ 8$ ; sp. gr. 0.79. Oxidizes extremely easy and direct by production of acetic acid. Chlorine and bromine drive it over into chloral and bromal  $(\text{C}_4\text{H}_3)\text{O}, \text{HO} = (\text{C}_4\text{Cl}_3)\text{O}, \text{HO}$ . If aldehyd be warmed with oxide of silver under water, metallic silver is pre-

Compounds of  
acetyl with oxy-  
gen.

Aldehyd.

precipitated, and in the solution is found a silver salt, which apparently consists of  $\text{AgO}, \text{AcO}_2$ ; if the solution of this salt be mixed with baryta water, and the whole warmed with the precipitated oxide of silver, the silver separates anew, and the solution contains acetate of baryta. Potassium brought together with aldehyd evolves hydrogen under the production of  $\text{KO}, \text{AcO}$ . If we warm the same with a solution of potassa, a brown resinous mass separates—the aldehyd resin.

If aldehyd be brought together with ammonia and hydro-sulphuric acid, a base is obtained, the *thialdin*, and, by the employment of hydroselenic acid, the *selenaldin*.

*Aldehyd-ammonia*:  $\text{NH}_4\text{O}, \text{AcO}$ , whose production was given above, crystallizes in colorless, transparent, shining, easily-broken crystals, possesses a peculiar odor, is volatile, easily inflammable, melts at  $80^\circ$ , and at  $100^\circ$  distills over unaltered, very soluble in water, soluble with difficulty in alcohol, and insoluble in ether. If we evaporate the watery solution of 1 part aldehyd-ammonia, and 1 part anhydrous hydrocyanic acid with hydrochloric acid, we obtain chloride of ammonium and *alanin*  $= \text{NC}_6\text{H}_7\text{O}_4 = (\text{NH}_2, \text{C}_6\text{H}_5)\text{O}_4$ .

*Transposing Products of Aldehyd*.—Aldehyd, inclosed in a tube, changes after some time into an agreeably-smelling fluid, which boils at  $81^\circ$ , does not oxidize in the air, and treated with potassa produces no resin. Aldehyd often changes, if it be preserved a long time in a closed vessel, into long, colorless, transparent prismatic columns of great lustre, while another part remains fluid, but at a lower temperature likewise becomes solid. The crystals of metaldehyd, solid at ordinary temperatures, are inodorous and tasteless, insoluble in water, but easily soluble in alcohol; they sublime at  $120^\circ$ , and consist of  $\text{C}_{12}\text{H}_{12}\text{O}_6$ . 3 atoms aldehyd have, therefore, changed to 1 atom metaldehyd; they easily fusible crystals have the same constitution; they smell slightly like aldehyd, are soluble in water, alcohol, and ether, melt at  $2^\circ$ , and boil at  $94^\circ$ ; are not affected by potassium and ammonia. If we conduct *hydrosulphuric acid* into a solution of aldehyd in water, there separates a thick water-clear oil, of strong garlic-like smell, and which consists of  $\text{C}_{12}\text{H}_{13}\text{S}_7 = \text{C}_{12}\text{H}_{12}\text{O}_6 + \text{HS}$ . If this oil be brought together with chloride of calcium, we obtain sulphide of calcium, and an evolution of aldehyd; treated with ammonia gas, it goes over into thialdin; if we add to this oil a few drops of sulphuric acid we obtain, accompanied by separation of hydrosulphuric acid, a crystalline body, which consists of  $\text{C}_{12}\text{H}_{12}\text{S}_6$ , and can be named *sulphometaldehyd*. If *sulphurous acid gas* be conducted into an alcoholic solution of aldehyd-ammonia, by strongly refrigerating, a richly crystalline precipitate is obtained of sharp taste, like sulphurous

Aldehyd-ammonia and sulphurous acid, and sulpho-carbonic acid.

Carbothialdin.

acid and aldehyd-ammonia. This body consists of  $\text{NC}_5\text{H}_5\text{S}_2\text{O}_6 = \text{NH}_4\text{O}, \text{C}_4\text{H}_3\text{O} + 2\text{SO}_2$ . *Sulphocarbonic acid*, brought into an alcoholic solution of aldehyd-ammonia, gives white shining crystals of *carbothialdin*  $= \text{NC}_5\text{H}_5\text{S}_2 = \text{NH}_3, \text{C}_5\text{H}_5\text{S}_2 = \text{NH}_3, (\text{C}_4\text{H}_3\text{O}, \text{CS}_2)$ .

*Hydrate of Acetyl* (hydrate of acetic acid):  $\text{HO}, \text{AcO}_3$ . Ordinary vinegar is obtained by the so-called acetic fermentation which consists of the change of alcohol to acetic acid. For this result are necessary: (1) alcohol diluted with water, (2) air, (3) co-operating substances which produce oxidation, as yeast, different organic substances which are found in the fermenting juices of plants, honey, leaven, vinegar itself; and (4) a temperature of 25 to 30°. For the production of vinegar it is important that the oxygen comes quickly in contact with the alcohol, *i. e.* that many points of contact between both be given, that the forming aldehyd can quickly oxidize (quick vinegar formation). To the production of acetic acid serves either, a mixture of brandy and water, or other fermented fluid, as grape-wine, fruit-wine, beer, etc. The raw vinegar is a mixture of water, acetic acid, different salts, gums, some ferment, etc. By distillation of raw vinegar we obtain rectified vinegar, which consists of a mixture of water and pure acetic acid; by saturation of the same with bases (potassa, soda, oxide of lead) and evaporation of the solution, acetic acid salts are obtained, and if the same, in a completely dry condition, be distilled with 1 atom hydrate of sulphuric acid, or with bisulphate of potassa, the hydrate of acetic acid is procured, however, mostly impure by sulphurous acid, which is absorbed by rectification over a little superoxide of lead. We obtain hydrate of acetic acid from the raw wood vinegar (*v.* wood-spirit), which is a mixture of water, acetic acid, wood-spirit, zylit, etc., and different empyreumatic oils, when we saturate the mixture with carbonate of lime. The empyreumatic oil which is separated is taken away, and afterwards the solution of impure acetate of lime is evaporated to the sp. gr. of 1.116, and then decomposed with sulphate of soda. The solution of acetate of soda is separated by pressing from the sulphate of lime, and brought to crystallization by evaporation. The crystals are cautiously heated in an iron kettle unto the complete destruction of the empyreumatic oil; by dissolving and re-crystallization we obtain pure acetate of soda, and from this by distillation with hydrate of sulphuric acid, the pure acetic acid. If we submit biacetate of potassa  $\text{KO}, \text{HO}, 2\text{AcO}_3$ , to a heat of 300°, it separates into simple acid salt and hydrate of acetic acid.

Properties of acetic acid.

The pure hydrate of acetic acid is a completely colorless fluid, of a penetrating agreeable acid smell, and very strong acid taste; at 13° it crystallizes in water-clear leaflets, which melt at 16°. (If the acetic acid be impure



with acetone, it does not crystallize.) Sp. gr. 1.0635; boiling point  $117^{\circ}$ . If the hydrate be heated to boiling, the vapor inflames. The hydrate mixes with water accompanied by evolution of heat and increase of density; the sp. gr. of a mixture of  $\text{HO}, \text{AcO}_3$ , with 2 atoms water, is 1.078; a greater addition of water produces no farther increase of density; a mixture of  $\text{HO}, \text{AcO}_3$ , with 9 atoms water, has again a sp. gr. of 1.0635, therefore equal to that of the hydrates.

If the vapor of acetic acid be conducted through a feebly glowing tube filled with pieces of coal, it partly separates into acetone ( $\text{C}_2\text{H}_5, \text{C}_4\text{H}_9$ ) $\text{O}_2$ , and carbonic acid; conduct the same over platinum black at  $200^{\circ}$ , and it is completely decomposed. Anhydrous acetate of alkalis (acetates of baryta and lead), submitted to dry distillation, give acetone and carbonic acid salts. A mixture of acetate of potash and arsenious acid, heated little by little, give oxide of kakodyl ( $\text{C}_4\text{H}_5\text{As}$ )O and carbonic acid. Distilled with *peroxide of manganese* and dilute *sulphuric acid*, we obtain formic acid; in like manner operate *iodic acid*, *superiodic*, and *chloric acid*; it reduces *chloride of gold*, but not the *oxide of mercury*. *Chlorine gas* conducts the acetic acid under the co-operation of light, first over into dichloroacetic acid  $\text{HO}(\text{C}_2\text{Cl}_2, \text{C}_2\text{H})\text{O}_3$ , and at last into chloroacetic acid  $\text{HO}(\text{C}_4\text{Cl}_3)\text{O}_3$ . Brought together with anhydrous sulphuric acid, sulphoacetic acid  $2\text{HO}(\text{C}_4\text{H}_2, \text{SO}_2)\text{O}_3, \text{SO}_3$ , is obtained. Acetic acid produces with bases neutral, basic, and acid salts; the most, however, are neutral; Acetic acid  
salts. they often crystallize with water, and most all are soluble in water, and many also in alcohol. The peroxide of silver and mercury salts are not easily soluble in water, and the salts of oxide of wolfram and of molybdenum are insoluble. They are obtained either direct or through double affinity. In its relation to oxide of mercury acetic acid differs from formic acid; furthermore, formic acid gives with magnesia and oxide of lead salts insoluble in alcohol, the acetic acid, on the contrary, soluble salts. Acetic acid salts give, by heating, acetone, formic do not. *Concentrated sulphuric acid* blackens the acetic acid salts by heating, which is not the case with formic acid.

*Acetate of Ammonia*:  $\text{NH}_4, \text{O}, \text{AcO}_3$ . By evaporating neutral acetates of ammonia, dissolved in water, in a vacuum over sulphuric acid, we obtain thin columns; and by evaporating the solution at a higher temperature radiated crystals of acid salts are obtained =  $\text{NH}_4, \text{O}, \text{HO}, 2\text{AcO}_3$ ; the same melts at  $76^{\circ}$  and sublimes at  $120^{\circ}$ . By shaking acetate of ethyl with aqueous ammonia *acetamid* is produced =  $\text{NH}_2\text{AcO}_2$ , and if acetate of ammonia be distilled with anhydrous phosphoric acid, the former goes over into *nitroacetyl*,  $\text{AcN}$ . The *potassa salt*,  $\text{KO}, \text{AcO}_3$ , forms a leafy deliquescent mass which easily melts, and during the cooling stiffens crystalline. The acid salt,  $\text{KO}, \text{HO}, 2\text{AcO}_3$ , is obtained if chlorine be brought into



a solution of the neutral salt or by supersaturation of the same with acetic acid and slow evaporation; flexible crystals, which at  $200^{\circ}$  separate into  $\text{KO}, \text{AcO}_3$ , and  $\text{HO}, \text{AcO}_3$ . The *neutral soda salt*  $\text{NaO}, \text{AcO}_3$  easily crystallizes with 6 atoms water; the crystals dissolve in 4 parts water, and effloresce in the air; at  $315^{\circ}$  the salt yet suffers no decomposition. The *baryta salt*,  $\text{BaO}, \text{AcO}_3 + 3\text{aq}$ , crystallizes in transparent prisms; soluble in an equal quantity of water. The *lime salt*,  $\text{CaO}, \text{AcO}_3$ , crystallizes in prismatic needles of a silky lustre which contain water and effloresce. The *alumina salt*,  $\text{Al}_2\text{O}_3, 3\text{AcO}_3$ , is procured by decomposition of sulphate of alumina by acetate of lead. Dries to a gum-like, deliquescent mass, soluble in water, and by heating loses acetic acid. Serves as a mordant in calico-printing. The salt of the *oxide of iron*,  $\text{Fe}_2\text{O}_3, 3\text{AcO}_3$ , appears as a red-brown, deliquescent, jelly-like mass. The *zinc salt*,  $\text{ZnO}, \text{AcO}_3$ , crystallizes in six-sided leaflets, separates by heating into  $\text{ZnO}, \text{HO}, 2\text{AcO}_3$ , which sublimes as woolly meal.

*Acetic Acid and Oxide of Lead.* *Sesquibasic Salt*,  $6\text{PbO} + \text{AcO}_3$ , is obtained if the neutral salt be a long time digested with 5 atoms oxide of lead; a white powder almost insoluble in water. *Tribasic salt*,  $3\text{PbO} + \text{AcO}_3$  (vinegar of lead), arises from the digestion of a solution of sugar of lead with 2 atoms oxide of lead; it remains behind after evaporation, an uncrystalline mass, easily soluble in water. *Sesqui-basic salt*,  $3\text{PbO} + 2\text{AcO}_3$ , remains behind if anhydrous sugar of lead be heated to  $280^{\circ}$ , accompanied by evolution of carbonic acid and aceton; crystallizes in leafy crystals of mother-of-pearl lustre. The *neutral salt* (sugar of lead),  $\text{PbO}, \text{AcO}_3 + 3\text{aq}$ , is obtained by dissolving oxide of lead in dilute acetic acid. Crystallizes in long four-sided prisms, sharpened by two faces; the crystals effloresce in the air, dissolve in  $1\frac{1}{2}$  parts water and in 8 parts alcohol; they melt at  $57^{\circ}$  in their water of crystallization, and lose the latter completely at  $100^{\circ}$ . Possesses a permanent sweet taste.

*Acetic Acid and Oxide of Copper.* Oxide of copper gives with acetic acid a neutral and several basic combinations. In commerce, under the name of verdigris, rust of brass, green gold, occur several basic salts; the same is obtained when wine-lees, already become acid, are interstratified with thin copper plates, and then moistened with a solution of verdigris. The verdigris is considered as a mixture of  $3\text{CuO} + 2\text{AcO}_3$  with  $3\text{CuO} + \text{AcO}_3$ , according as it separates into these compounds in contact with water. If the verdigris be dissolved in dilute acetic acid after evaporation, bluish green crystals are obtained, which consist of  $\text{CuO} + \text{AcO}_3 + \text{aq}$ . This neutral salt dissolves in 5 parts boiling water: in the cold, we obtain crystals with 6 atoms aq. If this neutral salt be brought together with plates of copper, and the whole exposed to the air a few months, we obtain the so-called blue verdigris, which consists of  $4\text{CuO} + \text{AcO}_3 + 6\text{aq}$ ; the

same separates in contact with water into  $3\text{CuO}, \text{AcO}_3$ , and  $\text{CuO}, \text{AcO}_3$ . If the compound  $3\text{CuO} + 2\text{AcO}_3$  be dissolved in boiling water a combination separates, which contains 48 atoms  $\text{CuO}$ , 1 atom  $\text{AcO}_3$ . *Acetate of protoxide of mercury*:  $\text{Hg}_2\text{O}, \text{AcO}_3$ , crystallizes in white flexible mica-like scales, which dissolve in 33 parts cold water. The silver salt:  $\text{AgO}, \text{AcO}_3$  crystallizes in leaflets having a mother-of-pearl lustre, and dissolves in 100 parts water.

*Oxysulphide of Acetyl*:  $\text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{S}_2 \end{smallmatrix} \right.$ , is obtained by the introduction of hydrosulphuric acid into oxychloride of acetyl; by distillation there go over, accompanied by evolution of hydrochloric acid, two fluids, which after a little time stiffen crystalline; one combination is oxysulphide of acetyl, the other oxysulphochloride of acetyl. The first possesses a feeble chloresulphur odor; it melts at  $120^\circ$ , insoluble in water, soluble in alcohol and ether; treated with potash, acetate of potash and sulphide of potassium are produced.

*Chloride of Acetyl*:  $\text{AcCl}_3$  is obtained by the action of chlorine upon chlorethyl. A colorless, easily-flowing fluid of ethereal odor and sweet taste; boils at  $75^\circ$ : sp. gr. 1.372. Decomposes by an alcoholic potash solution into acetate of potash and chloride of potassium. By the operation of chlorine under the influence of sunlight, we obtain at first a combination of chloride of acetyl with chloride of bichloracetyl  $(\text{C}_2\text{Cl}_2, \text{C}_2\text{H})\text{Cl}_3 + (\text{C}_4\text{H}_3)\text{Cl}_3 = \text{C}_4\text{H}_2\text{Cl}_4$ , then chloride of bichloracetyl, and at last chloride of chloracetyl  $(\text{C}_4\text{Cl}_3)\text{Cl}_3$ .

*Oxychloride of Acetyl*:  $\text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ , is obtained by the introduction of chlorine into oxide of ethyl, in the beginning at  $0^\circ$  and later in a higher temperature. A strongly acid yellow-smoking fluid is produced, if the same be heated a long time to  $100^\circ$ , and then distilled, oxychloride of acetyl remains behind, if the boiling point ascends to  $142^\circ$ . Transparent, not acid fluid, of fennel-like odor and taste; in contact with water, it decomposes into acetic and hydrochloric acid. By the action of potassium we obtain  $\text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix} \right.$ , non-volatile; sp. gr. 1.50; by chlorine in the sunlight it goes over into oxychloride of chloracetyl  $(\text{C}_4\text{Cl}_3) \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ .

*Oxysulphochloride of Acetyl*:  $\text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{S} \\ \text{Cl} \end{smallmatrix} \right.$  Its production, vide above, oxysulphide of acetyl. It forms yellow disagreeably smelling scales; separates, by an alcoholic solution of potassa, into chloride of potassium, sulphide of potassium, and acetate of potassa.

*Carbonate of Oxychloride of Acetyl*:  $\text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right. + \text{CO}_2$ , is pro-

duced by the action of chlorine in daylight upon carbonate of ethyl; colorless, heavy fluid; of sweet, peculiar smell.

*Formate of Oxychloride of Acetyl:*  $\text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} + \text{FoO}_3 \right.$ , is obtained by conducting chlorine into formate of ethyl. A transparent, feebly acid, aromatic-smelling and bitter-tasting fluid, soluble in water and in alcohol, of 1.261 sp. gr. Gives with potassa, chloride of potassium, acetate and formate of potassium.

*Acetate of Oxychloride of Formyl:*  $\text{Fo} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} + \text{AcO}_3 \right.$ . This combination metameric with the foregoing one is obtained by the action of chlorine upon acetate of methyl. Colorless, transparent fluid, of irritating vinegar odor, and sweetish garlic-like, later burning taste, boils at  $145^\circ$ ; sp. gr. 1.25; in contact with water, decomposes into formic, acetic, and hydrochloric acid.

*Acetate of Oxychloride of Acetyl:*  $\text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} + \text{AcO}_3 \right.$ , is, like the foregoing compound, obtained by the influence of chlorine upon acetate of ethyl; neutral fluid; boils at  $110^\circ$ ; sp. gr. 1.301; smells like acetic acid, is by the further action of chlorine, under the co-operation of sunlight, converted at last into  $(\text{C}_4\text{Cl}_3) \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} + (\text{C}_4\text{Cl}_3)\text{O}_3 \right.$ .

*Acetate of Oxychloride of Chlorformyl:*  $(\text{C}_2\text{Cl}) \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} + \text{AcO}_3 \right.$ . Chlorine is conducted through acetate of methyl until no more hydrochloric acid is evolved.

Water-clear liquid, heavier than water, boils at  $143^\circ$ , smells like peppermint, soluble in alcohol and in ether.

*Nitro-acetyl* (Cyanmethyl, Acetonitryl):  $\text{AcN}$ . Acetyl and nitrogen. Acetate of ammonia is distilled with anhydrous phosphoric acid, or cyanide of potassium is distilled with sulphate of methyl:  $\text{C}_2\text{H}_3 + \text{NC}_2 = \text{C}_4\text{H}_3 + \text{N}$ . Water-clear, not poisonous, agreeably-tasting fluid; boils at  $77^\circ$ , gives by treatment with aqueous potassa, ammonia and acetate of potassa, and with potassium, cyanide of potassium and methyl.

*Acetyl-Platinchloride, Plantinchloride* (*Chlorplatin-acetylchlorur*):  $(\text{Ac}, \text{PtCl})\text{PtCl}$ . Acetyl and chloride of platinum. A mixture of 1 part chloride of platinum with 6 parts alcohol is distilled to  $\frac{1}{6}$ th. To the brown residual clear fluid is added  $\frac{1}{11}$ ths platinchloride of ammonium; by evaporation crystals are obtained, which consist of chloride of ammonium and platinchloride—acetyl-platinchloride, which by recrystallization are purified. A very concentrated solution of this salt is mixed with a solution of chlorplatinum so long as a precipitate is produced. After this it is filtered, and the filtrate evaporated in a vacuum. Pale citron-yellow powder, which is soon black, and is soluble in alcohol and in ether. Heated over a free fire, it

burns accompanied by separation of platinum. The watery solution soon decomposes, accompanied by evolution of gas and deposition of platinum; addition of hydrochloric acid prevents the decomposition; if into the solution nitrate of silver be dropped, chloride of silver is precipitated, and from the fluid separated from the precipitate platinum black soon falls; if the platinum black be removed by filtration, silver salts again produce a precipitation of chloride of silver. Platinchloride of chlorplatinacetyl combines with chloride of potassium, of sodium, and of ammonium, forming nitrous compounds, which crystallize in beautiful yellow crystals; with ammonia it goes also into a combination which appears as yellow powder.

b. *Derived radicals.*

a. Bichloracetyl =  $C_2Cl_2, C_2H = C_4Cl_2H$ .

*Bichloroacetic Acid*:  $HO(C_2Cl_2, C_2H)O_3$ , is known only in combination with hydrate of acetic acid. This combination  $2HO(C_4Cl_2H)O_3, \text{Ac}O_3$  is obtained by the first action of chlorine upon hydrate of acetic acid in the shade. Colorless fluid, of the odor of hydrate of acetic acid. By further operation of chlorine in sunlight, is converted into chloroacetic acid.

Bichloroacetyl  
compounds.

*Bichloroacetate of Oxychloride of Formyl*:  $Fo \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} + (C_4Cl_2H)O_3 \right.$ , arises by the decomposition of acetate of oxychloride of formyl by means of chlorine. Little known.

*Bichloroacetate of Oxychloride of Chlorformyl*:  $(C_2Cl) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} + (C_4Cl_2H)O_3 \right.$ , is obtained by the action of chlorine upon the former combination.

*Formate of Oxychloride of Bichloroacetyl*:  $(C_4Cl_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} + Fo \right.$ , arises by the action of chlorine upon formate of ethyl.

*Acetate of Oxychloride of Bichloroacetyl*:  $(C_4Cl_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} + AeO_3 \right.$ , is produced by the action of chlorine upon acetate of oxychloride of acetyl, under the co-operation of sunlight. Oily fluid, of 1.485 sp. gr. By the first action of chlorine, 1 atom of acetate of oxychloride of acetyl remains undecomposed, whereby a combination is obtained, which consists of  $C_4H_5Cl_3O_4$ ; the same is colorless, oily, smells agreeably, like peppermint; boils at  $164^\circ$ , sp. gr. 1.367.

$\beta$ . Chloroacetyl =  $C_2Cl_2, C_2Cl = C_4Cl_3$ .

Chloroacetyl.

*Oxide of Chloroacetyl*:  $(C_4Cl_3)O$ , if a mixture of 50 parts sulphide of potassium (KS), 16 parts oxychloride of chloroacetyl  $(C_4Cl_3) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$  and 200 parts alcohol be distilled, there is obtained, accompanied by separa-

Compounds of  
the same with  
oxygen.



tion of sulphur and chloride of potassium, an oily, garlic-like smelling fluid, which after purification with potassium and nitric acid, exhibits a colorless, sweet-tasting liquid, smelling like *Spirea Ulmaria*, of sp. gr. 1.654; point of ebullition  $210^{\circ}$ . Insoluble in water, easily soluble in alcohol and ether. Combines with chlorine in sunlight, producing oxychloride of chloracetyl; if water be present at the same time, we obtain chloracetic acid. Bromine gives with the same oxybromide of chloracetyl.

*Oxyhydrate of Chloracetyl* (Chloral):  $\text{HO}(\text{C}_4\text{Cl}_3)\text{O}$ , is produced by the action of chlorine upon absolute alcohol and aldehyd, as well as by the decomposition of starch or sugar by chlorine. Chlorine is conducted into alcohol until, by elevation of temperature, no further escape of hydrochloric acid is observed. At last a syrup-thick fluid remains, which is mixed with three times its weight of sulphuric acid, the mixture distilled, and the distillate subjected to a new distillation for the removal of the hydrochloric acid. When the boiling point rises from  $90$  to  $94^{\circ}$ , the distillation is interrupted, and the residue, freed from hydrochloric acid, repeatedly distilled with sulphuric acid; the chloral thus purified, is afterwards rectified over some quicklime. Colorless, oily fluid, of a peculiar penetrating odor, exciting copious effusion of tears; almost tasteless: easily soluble in water, alcohol, and ether; has not an acid reaction; sp. gr. 1.502; point of ebullition  $92^{\circ}$ . If chloral be shaken with a little water, there is produced, accompanied with evolution of heat, a white crystalline mass—hydrate of chloral.

If the same be heated with sulphuric acid, there is obtained, accompanied by evolution of hydrochloric and carbonic acid, nearly water-free chloral, the *chloralid*  $\text{C}_{10}\text{H}_2\text{Cl}_6\text{O}_2$ , which crystallizes in water-clear prisms, of a glass lustre, and grouped in the form of a star; the same fuses at  $120^{\circ}$ , is tasteless, but in the alcohol solution, tastes sharp and caustic, and by warming possesses an odor resembling chloral; by being dissolved in potassa, the chloral decomposes into formic acid and chloride of formyl: fuming nitric acid oxidizes the same, producing chloracetylic acid. By long standing in a closed bottle, chloral changes like aldehyd, into a white amorphous, porcelain-like mass, insoluble in water, is named *insoluble chloral*, and is metameric with chloral; if the same be cautiously heated to  $200^{\circ}$ , it is converted into fluid chloral.

*Chloracetic Acid* is obtained by the complete decomposition of hydrate of acetic acid by chlorine under the influence of sunlight. Not more than nine decigrammes of acid are permitted to be applied to one quart of chlorine gas. The chloracetic acid deposits itself crystalline on the sides of the glass; at the same time is produced oxalic acid. It is also obtained by oxidation of chloral, and by the action of sunlight upon a mixture of terchloride of chloracetyl  $(\text{C}_4\text{Cl}_3)\text{Cl}_3$  with water. Crystallizes in beautiful rhombohedrals; colorless, of feeble odor, and bitter biting taste, deliquesces

in the air, colors the tongue white, and, brought upon the skin, produces blisters; the vapor is irritating and suffocating; fuses at  $48^{\circ}$ ; boils at  $195^{\circ}$ ; sp. gr. 1.617. If the watery solution of the acid be brought together with potassa amalgam, potassa and acetate of potassa are obtained without evolution of gas. Heated with an excess of potassa or ammonia, it decomposes into carbonic acid and chloride of formyl. Chloracetic acid is very strong, and with bases produces crystalline salts. The *silver salt*  $\text{AgO}(\text{C}_4\text{Cl}_2)\text{O}_3$  appears in gray leaflets; if the *ammonia salt* be distilled with anhydrous phosphoric acid, we obtain nitrochloracetyl  $(\text{C}_4\text{Cl}_3)\text{N}$ .

*Chloride of Chloracetyl*:  $(\text{C}_4\text{Cl}_3)\text{Cl}$ . In the heat trichloride of chloracetyl falls into chloride of chloracetyl; it is also produced if an alcoholic solution of trichloride of chloracetyl be distilled with KS, HS, and the production is accompanied by separation of chloride of potassium. Fluid water-clear, insoluble in water, soluble in alcohol, and in ether; boils at  $122^{\circ}$ ; sp. gr. 1.699; combines directly with chlorine and bromine, forming  $(\text{C}_4\text{Cl}_3)\text{Cl}_3$  and  $(\text{C}_4\text{Cl}_3)\left\{\begin{smallmatrix} \text{Cl} \\ \text{Br}_2 \end{smallmatrix}\right.$  Chloracetyl and chlorine.

*Tetrachloride of Chloracetyl* (Sesquichloride of Carbon):  $(\text{C}_4\text{Cl}_3)\text{Cl}_3$ . This combination arises by the action of chlorine upon chlorethyl, upon chloride of acetyl, upon chlorethyl, etc., under the co-operation of sunlight.

It is most easily obtained if some chlorethyl be brought into a bottle filled with dry chlorine gas, and the whole left standing a long time, first in the shade and then in the sun. Water-clear, direct, rhombic prisms; sp. gr. 2.00; fuses at  $160^{\circ}$ , and boils at  $182^{\circ}$ ; possesses the hardness of sugar, is easily pulverized, possesses a strong camphor-like smell, is scarcely soluble in water, easily soluble in alcohol and ether. With amalgam of potassium and water gives chloride of potassium and acetate of potassa. Heated with iodine, phosphorus, or sulphur, loses 2 atoms chlorine, and produces protochloride of chloracetyl.

*Oxychloride of Chloracetyl* (Chloraldehyd):  $(\text{C}_4\text{Cl}_3)\left\{\begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix}\right.$  is obtained simultaneously with trichloride of chloracetyl, if oxychloride of chloracetyl be exposed to a temperature of  $300^{\circ}$ ;  $2(\text{C}_4\text{Cl}_3)\left\{\begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix}\right. = (\text{C}_4\text{Cl}_3)\left\{\begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix}\right. + (\text{C}_4\text{Cl}_3)\text{Cl}_3$ . Colorless fluid, which fumes copiously in the air, and, in a moist condition, strongly reddens litmus. Placed upon the tongue, produces the feeling of dryness, then strong burning, and leaves a white spot; boils at  $118^{\circ}$ ; sp. gr. 1.603. The same combination is also obtained if chlorformate of oxychloride of chloracetyl,  $(\text{C}_4\text{Cl}_3)\left\{\begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix}\right. + (\text{C}_2\text{Cl})\text{O}_3$  be conducted through a glowing tube. In contact with water it decomposes into chloracetic and hydrochloric acid. Brought to-

gether with *ammonia* we obtain chloride of ammonium, and *chloracetamid* =  $\text{NH}_2(\text{C}_4\text{Cl}_3)_2\text{O}_2$ ; with phosphide of hydrogen, arises the corresponding phosphorous combination:  $\text{PH}_2(\text{C}_4\text{Cl}_3)_2\text{O}_2$ , in form of white, loose crystal scales, of garlic odor and bitterish taste.

*Oxybichloride of Chloracetyl*:  $(\text{C}_4\text{Cl}_3)_2 \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ , is obtained by the action of chlorine upon oxychloride of acetyl, under the co-operation of sunlight, as well as by the direct union of oxide of chloracetyl with chlorine. Solid; fuses at  $69^\circ$ ; boils at  $180^\circ$ ; crystalline, decomposes at high temperature, producing the former combination and terchloride of chloracetyl, and, in contact with sulphide of potassium and alcohol, gives oxide of chloracetyl.

*Sulphochloride of Chloracetyl*:  $(\text{C}_4\text{Cl}_3)_2 \left\{ \begin{smallmatrix} \text{S} \\ \text{Cl}_2 \end{smallmatrix} \right.$ , arises by the operation of chlorine upon sulpho-chloride of acetyl.

*Oxybromide of Chloracetyl*:  $(\text{C}_4\text{Cl}_3)_2 \left\{ \begin{smallmatrix} \text{O} \\ \text{Br}_2 \end{smallmatrix} \right.$ . Oxide of chloracetyl is exposed a few days with bromine to the sunlight. Colorless, inodorous crystals, which fuse at  $96^\circ$ , and, at  $180^\circ$ , decompose into oxide of chloracetyl and bromine.

*Chlorbromide of Chloracetyl*:  $(\text{C}_4\text{Cl}_3)_2 \left\{ \begin{smallmatrix} \text{Cl} \\ \text{Br}_2 \end{smallmatrix} \right.$ . Protochloride of chloracetyl combines directly with bromine; crystalline compound of 2.3 sp. gr.; at  $200^\circ$  decomposes into protochloride of chloracetyl and bromine; likewise, by treatment with sulphide of potassium, accompanied by separation of sulphur, and production of bromide of potassium.

*Carbonate of Oxybichloride of Chloracetyl*:  $(\text{C}_4\text{Cl}_3)_2 \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right. + \text{CO}_2$ . Carbonate of oxychloride of acetyl with chlorine, left in contact under the co-operation of sunlight, is soon converted into carbonate of oxychloride of chloracetyl. Snow white, small needles; fuses at  $85^\circ$ , and stiffens at  $63^\circ$ , to a crystalline mass. Decomposes, by heating, partially into carbonic acid, oxychloride of chloracetyl, and terchloride of chloracetyl.

Brought together with ammonia gas, we obtain, accompanied by evolution of heat, a soft mass, which by heating throws out a thick cloud, whilst a brown substance remains behind, which consists of chloride of ammonium, and some othersalts beside *chlorcarbæthamid*. The last can be extracted by ether. Chlorcarbæthamid produces white, fatty, inflammable, crystal scales, which fuse at  $136^\circ$ , and quickly heated volatilize without decomposition; it consists of  $2(\text{N H}_2, 2\text{CO}) + \text{NH}_2, 2(\text{C}_4\text{Cl}_3)_2 \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right.$

If this compound be digested a few days with aqueous ammonia, we obtain, after evaporation of the solution, a salt of white, fatty, inflammable scales, which fuse at  $37^\circ$ , and are easily soluble in water, in alcohol, and in ether.

This salt is chlorcarbæthamate of ammonia, and consists of  $2\text{NH} + \text{O}(\text{C}_{10}\text{H}_4\text{NCl}_7\text{O}_7$ .

*Formate of Oxybichloride of Chloracetyl:*  $(\text{C}_4\text{Cl}_3) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 + \text{FoO}_3. \end{array} \right.$

Formate of oxybichloride of acetyl by further action of chlorine, changes at first into formate of chloracetyloxy-bichlorid and then into

*Chlorformate of Oxybichloride of Chloracetyl*  $(\text{C}_4\text{Cl}_3) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 + (\text{C}_2\text{Cl})\text{O}_3. \end{array} \right.$  Water-clear fluid, of suffocating odor, and a stringent, insupportable acid taste. Sp. gr. 1.705; point of ebullition  $300^\circ$ . Conducted through a glowing tube, decomposes into  $(\text{C}_4\text{Cl}_3) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 \end{array} \right.$  and  $2(\text{C}_2\text{Cl}) \left\{ \begin{array}{l} \text{Cl} \\ \text{O}_2. \end{array} \right.$

With ammonia gas it gives chloracetamid; and, treated with hydrous potassa, chloracetate of potassa, chloride of potassium, and carbonate of potassa.

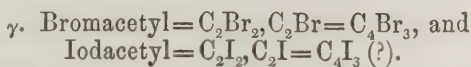
Brought together with wood-spirit or alcohol, we obtain chloracetic acid and chlorformate of methyl or ethyl, accompanied by simultaneous production of hydrochloric acid.

*Acetate of Oxybichloride of Chloracetyl:*  $(\text{C}_4\text{Cl}_3) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 + \text{AcO}_3, \end{array} \right.$  is obtained by the action of chlorine in absence of sunlight upon acetate of terchloride of acetyl. Gives with potassa acetate and chloracetate of potassa, besides chloride of potassium.

*Bichloracetate of Oxybichloride of Chloracetyl*  $(\text{C}_4\text{Cl}_3) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 + (\text{C}_2\text{Cl}_2, \text{C}_2\text{H})\text{O}_3. \end{array} \right.$  The former compound, by the further action of chlorine, changes first into this compound, and, under the effect of sunlight, into

*Chloracetate of Oxybichloride of Chloracetyl,*  $(\text{C}_4\text{Cl}_3) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 + (\text{C}_4\text{Cl}_3)\text{O}_3. \end{array} \right.$  Colorless oil, of strong, penetrating, chloral odor and burning taste. Gives with nitrate of silver a white precipitate of chloride of silver. Sp. gr. 1.79; boils at  $245^\circ$ ; will, in sunlight, change into  $(\text{C}_4\text{Cl}_3)\text{Cl}_3$ . At a high temperature decomposes into oxide of chloracetyl, and in contact with water separates at once into chloracetic and hydrochloric acid. Brought into contact with alcohol, chloracetate of oxide of ethyl is obtained.

*Nitrochloracetyl:*  $(\text{C}_4\text{Cl}_3)\text{N}$ . Is obtained by distillation of chloracetate of ammonia with water-free phosphoric acid. Fluid; sp. gr. 1.444; boiling point  $81^\circ$ ; treated with potassa, gives ammonia and chloracetate of potassa.



*Oxyhydrate of Bromacetyl (Bromal):*  $\text{HO}(\text{C}_4\text{Br}_3)\text{O}$ . To 1 part



water-free alcohol (or ether) are gradually added 4 parts bromine, and after 11 or 12 days the mixture distilled away to  $\frac{2}{3}$ ths, there escapes hydrobromic acid, bromethyl, and the so-called heavy bromide ether. The residue is dissolved in water, and the solution left to spontaneous evaporation. We obtain remarkably large crystals of hydrate of bromal, which, by distillation with hydrate of sulphuric acid, leave pure bromal. Oily fluid, completely transparent, strongly refracts light, of a tear-exciting odor, and sharp burning taste. Soluble in water, alcohol, and ether; from the watery solution hydrate of bromal crystallizes. By treatment with an aqueous solution of potassa it is decomposed, by complete transformation, into formic acid and bromide of formyl.

*Oxyhydrate of Iodacetyl* (Iodal):  $\text{HO}(\text{C}_4\text{I}_3)\text{O}(\text{?})$ , will be obtained by the action of iodine upon a mixture of equal parts of alcohol and nitric acid. An oil is deposited which is considered idal.

*Sulphacetyl*:  $\text{C}_4\text{H}_2\text{SO}_2$ .

*Sulphacetyl Sulphuric Acid* (Sulphacetic Acid):  $2\text{HO}(\text{C}_4\text{H}_2\text{SO}_2)\text{O}_3, \text{SO}_3$ . This paired double acid is obtained by introduction of vapor of anhydrous sulphuric acid into the hydrate of acetic acid. After reaction ceases, the mass, diluted with water, is saturated with carbonate of lead; from the solution the oxide of lead is precipitated by hydro-sulphuric acid, and by evaporation in a vacuum the anhydrous acid is procured. Crystallizes by low temperature in white, transparent prisms, which contain 3 atoms water of crystallization; it possesses a strong acid taste, similar to tartaric acid; deliquescent; fuses at  $62^\circ$ , and completely decomposes at a high temperature.

The acid saturates 2 atoms base; its salts are mostly soluble in water, and completely decompose at high temperatures. The *potassa salt* forms small crystals; the *silver salt* small transparent prisms.

#### PAIRED COMBINATIONS OF ACETYL.

*Acryl*:  $\text{Acr}=\text{C}_2, \text{C}_4\text{H}_3=\text{C}_4\text{H}_2, \text{C}_2\text{H}=\text{C}_6\text{H}_3$ .

*Production*.—Acryl is produced by dry distillation of glycerin as well as by the distillation of all fats which contain oxide of glycyl as base.

*Oxyhydrate of Acryl* (Acrolein),  $\text{HO}, \text{AcrO}$ , is obtained when a mixture of glycerin with acid sulphate of potassa is exposed to a high temperature. The distillation is conducted in a flask, which is connected with a receiver by means of a good cooling apparatus; from the receiver goes a gas-conducting tube, through which the evolved vapor escapes into the atmosphere. The distillate consists of an aqueous acid fluid which contains sulphurous acid, acric acid, and acrolein. The whole fluid is digested with oxide of lead till

the acid reaction vanishes, and then rectified upon the water bath. The acrolein distils over even below  $100^{\circ}$ , and may be freed from water by completely neutral chloride of calcium. A water-clear, colorless fluid, strongly refracting light, and attacking the eyes and nose frightfully; taste biting, burning; boils at  $52^{\circ}$ ; is lighter than water; dissolves in 40 parts water, easily soluble in alcohol and ether. In the air acrolein oxidizes very quickly, and produces disacryl, acric, acetic, and formic acid. The production of disacryl follows also exclusion of air. Chlorine and bromine form oily, heavy, etheric products. Acrolein decomposes by the operation of alkaline bodies, in the same manner as aldehyd, accompanied by the production of different resinous bodies.

*Acrolein-ammonia*:  $\text{NH}_4\text{O} + \text{AcrO}$ , is obtained if the etheric solution of acrolein be shaken with aqueous ammonia; falls as a white, crystalline, inodorous, indifferent body.

*Hydrate of Acrylic Acid*:  $\text{HO}, \text{AcrO}_3$ . If the aqueous solution of acrolein be mixed with nitrate of silver, a white precipitate is produced, which apparently consists of  $\text{AgO}, \text{AcrO}_3$ . Acrylate of silver is most conveniently produced, as we procure it by distillation of fat, when we bring in contact with nitrate of silver what goes over by rectification between  $40^{\circ}$  to  $60^{\circ}$ , and purify the salt by recrystallization. We slowly decompose the silver salt by hydrosulphuric acid, and distil the acric acid by a gentle heat. Water-clear fluid, smelling agreeably, like acetic acid, tastes purely acid, and dissolves in water in all proportions. If it be treated a long time with alkaline bases we obtain acetic acid salts  $2(\text{C}_6\text{H}_3\text{O}_3) + 3\text{HO} = 3(\text{C}_4\text{H}_3\text{O}_3)$ . Nitric acid converts it into formic acid and acetic acid,  $\text{C}_6\text{H}_3\text{O}_3 + \text{HO} + \text{O}_2 = (\text{C}_2\text{H})\text{O}_3 + (\text{C}_4\text{H}_3)\text{O}_3$ . The *soda salts* crystallize in transparent prisms of the size of lentils; the crystals contain 3 atoms aq., effloresce in the air, and possess a salty, bitter taste. The *baryta salt* dries to a gum-like mass. The *silver salt* crystallizes like the acetate of silver, and is with difficulty soluble in cold water.

*Disacryl*:  $\text{C}_{10}\text{H}_7\text{O}_4$ , exhibits a fine, loose, white, uncrystalline powder, inodorous and tasteless, insoluble in water, alcohol, and ether, and becomes strongly electric by rubbing.

*Lactyl*:  $\text{La} = \text{C}_4\text{H}_4\text{O}_2, \text{C}_2\text{H} = \text{C}_2\text{H}_2\text{O}_2, \text{C}_4\text{H}_3 = \text{C}_6\text{H}_5\text{O}_2$ . *Lactyl*.

*Lactic Acid*:  $\text{LaO}_5 = \text{C}_2\text{H}_2\text{O}_2(\text{C}_4\text{H}_3)\text{O}_3$ .

*Production*.—When we let nitric acid act upon alanin  $\text{NC}_6\text{H}_7\text{O}_4$ , we obtain lactic acid, nitrogen being evolved and water produced  $\text{NC}_6\text{H}_7\text{O}_4 + \text{NO}_3 = \text{C}_6\text{H}_5\text{O}_5 + 2\text{N} + 2\text{HO}$ .

Lactic acid is found in all animal fluids, and is produced by the so-called lactic acid fermentation; it is thence found in the acid liquor of sourkrout, sour cucumber juice, in meal paste become acid, in sour milk, in sour rice-water, sour tan liquor, etc. etc.

If the hydrate of lactic acid be heated to  $130^{\circ}$ , the *anhydrous*

*acid* distils over. This is solid, fusible, strongly bitter, almost insoluble in water, but soluble in alcohol and ether, and in contact with water is converted into hydrate. The anhydrous lactic acid gives with *ammonia gas* a combination in which the ammonia cannot be detected by the ordinary reagents.

*Hydrate of Lactic Acid:*  $\text{HO,LaO}_5$ , is best obtained by fermentation of milk sugar. In an earthen vessel holding 3 quarts we put 250 grammes milk sugar, 200 grammes chalk, 1 quart skimmed milk, and 2 quarts water. The mixture is exposed to a temperature of 25 to 30°, and often stirred; after ten or twelve days the fermentation is terminated. The mass is afterwards boiled in a kettle a quarter of an hour: from the hot filtered liquid the lactate of lime separates itself after the cooling, and is purified by recrystallization. By decomposition of the lactate of lime by sulphuric or oxalic acid, the pure lactic acid is obtained. It appears in its pure condition as a colorless, syrup-thick fluid, of 1.215 sp. gr., inodorous, of strong acid taste; mixes in all proportions with water and alcohol; also slightly soluble in ether. Two drops of lactic acid bring 100 grammes milk to coagulation; it coagulates white of egg, and dissolves phosphate of lime in considerable quantities. By *dry distillation* lactic acid decomposes into carbonic oxide, carbonic acid, *lactid*  $\text{C}_6\text{H}_4\text{O}_4$ , citraconic acid and aldehyd.

*Lactic Acid Salts.*—Lactic acid expels acetic acid from its compounds. Most of the lactic acid salts are soluble in water, and many possess the capability of crystallization. If the *dry lactate of copper* be heated to 200° or 210°, it decomposes into metallic copper, aldehyd, and carbonic acid. If we distil *lactate of protoxid of iron* with peroxide of manganese and sulphuric acid, we obtain aldehyd; and if chloride of sodium be present, at the same time, chloral. The *alkali salts* do not crystallize. The *zinc salt*,  $\text{ZnO,LaO}_5 + 3\text{aq}$ , is with difficulty soluble in water, and crystallizes in fine prisms, uniting so as to form crusts. The *protoxide of iron salt*,  $\text{FeO,LaO}_5 + 3\text{aq}$ , produces white needles, soluble with difficulty in water, and changeless in the atmosphere. The *copper salt* crystallizes in beautiful blue prisms.

*Lactid:*  $\text{C}_6\text{H}_4\text{O}_4 = (\text{C}_4\text{H}_3)\text{O}, \text{C}_2\text{H}_3\text{O}_3$ . Inodorous crystals, tasting slightly acid, which at 107° fuse, and at 250° boil. The watery solution is converted by degrees into lactic acid. If aqueous ammonia be allowed to act upon lactid, we obtain *lactamid*  $\text{NH}_3, \text{C}_6\text{H}_4\text{O}_4$ , in which by the ordinary reagents ammonia cannot be detected; at 100° aqueous potassa is, under pressure, converted into lactate of potassa, whereby lactamid differs from alanin.

*Chlorsuccyl:*  $\text{C}_2\text{H}_2, \text{C}_4\text{Cl}_3 = \text{C}_6\text{H}_2\text{Cl}_3$ .

*Chlorsuccinic Acid:*  $(\text{C}_2\text{H}_2, \text{C}_3\text{Cl}_3)\text{O}_3$ . By action of chlorine upon succinate of ethyl, a combination is obtained, which consists



of  $C_{16}H_{13}O_8$  (s. succinic acid). If the combination be heated to  $290^\circ$ , carbonic acid is evolved, whilst a smoking oily fluid distils over; if water be poured over the same, hydrochloric, chloracetic, and chloresuccinic acid are obtained. The last appears as a colorless crystalline mass, which fuses at  $60^\circ$ , is sublimable, tastes strongly acid, and leaves upon the tongue a white spot. The *ammonia salt* forms long asbestiform crystals; the *silver salt* exhibits fine shining needles.

*Acetonyl*:  $AO = C_2H_3, \text{ } ^\wedge C_4H_3 = C_6H_6 \rightleftharpoons Me, \text{ } ^\wedge Ac.$   
*Methylacetyl*.

*Oxide of Acetonyl* (Aceton):  $AO_2 = MeAcO_2 = 4$  volumes gas.

*Production*.—The oxide of Acetonyl is produced by the dry distillation of acetic acid; 2 atoms decompose in the following manner: from 1 atom acetic acid  $(C_2H_2, C_2H)O_3$  escape  $C_2O_3$ , whilst  $C_2H_2$  with H produce methyl; simultaneously  $C_2O_3$  take 1 atom O from the second atom acetic acid, thus producing 2 atoms carbonic acid, whereby arises  $(C_2H_2, C_2H)O_2$ , which with methyl exhibits oxide of acetonyl.

Dry acetate of lime is submitted to dry distillation in a retort, which is connected with several bottles kept cold. The distillate obtained, which consists of water, some acetic acid, acetone, and other empyreumatic products, is repeatedly distilled over a water-bath, then rectified over quicklime, and at last over chloride of calcium; or, we heat a quantity of pure unslaked lime with 2 parts dry acetate of lead, and purify the distillate in the same manner. In its pure condition, acetone exhibits an ethereal, entirely colorless fluid, of an agreeable, penetrating, volatile odor, and peculiar, burning, camphor-like taste; mixes with water, alcohol, and ether in every proportion; chloride of calcium and potassa separate it from the watery solution; it burns with strong luminous flame; point of ebullition  $55^\circ.6$ ; sp. gr. 0.7921. If acetone be conducted over *glowing hydrate of potassa*, it decomposes into hydro-methyl, carbonic acid, and hydrogen,  $C_6H_6O_2 + 4HO = C_2H_3, H + 2CO_2 + 6H$ . If we treat it with *acid chromate of potassa*, it divides completely into acetic and carbonic acid. Concentrated nitric acid decomposes acetone with violence, and produces the so-named mesitylid-aldehyde  $(C_2, ^\wedge C_4H_3)O + HO$ . By the operation of *chlorine*, we at last obtain mesityl-chloral,  $C_6H_4Cl_2O_2 = (C_2H)Cl + (C_4H_3) \left\{ \begin{array}{l} Cl \\ O_2 \end{array} \right. (?)$ . If we mix equal parts of *acetone* and *hydrate of sulphuric acid*, accompanied by constant diminution of the evolved heat, we obtain a dark brown mass, and if the same be mixed with double volume of water, there separates upon the surface oxide of mesityl  $= C_6H_5O = (C_2H_2, ^\wedge C_4H_3)O = (C_4H_2, ^\wedge C_2H_3)O$ . When we distil 2 volumes acetone with 1 volume hydrate of sulphuric acid by gentle heat, we obtain mesitylene  $C_{18}H_{12}$ , which behaves



to the aceton radical as metaldehyd to aldehyd. Potash lye acts upon aceton neither in the cold nor heat. The aceton swims upon the lye without mixing with it; but when left several days thoroughly mixed with hydrate of potassa, complete decomposition occurs; by mixture with water xylitole separates, and in the solution are found acetate of potassa, aceton, and wood-spirit. Potassium reacts powerfully upon aceton without evolution of permanent gases; the same products are formed, as by the action of potassa.

*Oxide of Mesityl:*  $C_6H_6O = (C_2H_2, \frown C_4H_3)O$  or  $(C_4H_2, \frown C_2H_3)O$ . Colorless, clear fluid, of aromatic odor similar to the oil of peppermint; insoluble in water; easily soluble in alcohol; burns with a luminous flame; boils at  $120^\circ$ .

*Simple Mesityloxydsulphuric Acid:*  $HO(C_6H_5O)\frown SO_3$ . In small quantities are mixed 2 volumes aceton to 1 volume hydrate of sulphuric acid, the solution diluted with water and saturated with baryta. From the baryta salt remaining dissolved the baryta is precipitated by sulphuric acid; if the solution of the acid be evaporated, it decomposes into sulphuric acid and oxide of mesityl. The baryta salt crystallizes in fine needles.

*Double Mesityloxydsulphuric Acid:*  $2HO(C_6H_5O)\frown 2SO_3$ , is like the former compound obtained by mixing equal volumes aceton and sulphuric acid. Known only in the aqueous solution. Oxide of mesityl also gives, with *phosphoric acid*, an acid combination  $(C_6H_5O)\frown PO_5$ .

*Mesityloxyd-chlorplatinum:*  $(C_6H_5O)\frown PtCl$ , is obtained by action of protochloride of platinum upon aceton. Forms small sulphur-yellow, inodorous, and metallic-tasting crystals. In small quantity soluble in water, alcohol, and ether. If the combination be boiled a long time in water, a black pulveriform body is precipitated, the *acechlor-platin-oxide*, which must consist of  $C_2H_2Pt$ . The pure *alkalies* completely decompose the compound.

*Chlormesityl:*  $(C_6H_5)Cl = (C_2H_2, \frown C_4H_3)Cl = (C_4H_2, \frown C_2H_3)Cl$ . To chloride of phosphorus we add aceton in small quantities, and afterwards water by drops, accompanied by refrigeration. By distillation there goes over after the termination of the decomposition, a heavy, slightly colored fluid. *Iodmesityl:*  $(C_6H_5)I$ , is obtained by the action of iodine and phosphorus upon aceton. Colorless, oily, very easily decomposed fluid. *Sulphomesityl* is said to be a volatile body of offensive odor.

*Oxyhydrate of Mesitylid:*  $C_6H_3O + HO = (C_2, \frown C_4H_3)O, HO = (C_4, \frown C_2H_3)O, HO$ . This compound is produced by the action of nitric acid upon aceton; a reddish-yellow, thick, heavy fluid, of sweetish penetrating odor; scarcely soluble in water. At the same time arises another compound  $= C_6H_3O + NO_3$ ; the same is a thick fluid, heavier than water, of penetrating sweetish odor and taste. If phosphorus be permitted to act upon aceton different acids are produced, as: *acephoric*, *phosphacetic*, and *acephosgenic acid*;

likewise by the common action of sulphur and ammonia upon acetone, are obtained different bodies not yet analyzed.

## SECOND MEMBER.

## PROPIONYL.

METACETYL. Primary Radical  $\text{Pr.} = 2\text{C}_2\text{H}_2, \text{C}_2\text{H} = \text{C}_6\text{H}_5$ .

*Production.*—The propionyl is produced in many different ways; Cyanogen and ethyl, by transposition, produce nitro-propionyl:  $2\text{C}_2\text{H}_2, \text{H} + \text{C}_2\text{N} = (2\text{C}_2\text{H}_2, \text{C}_2\text{H})\text{N}$ ; further, it arises by heating sugar, gum, starch, etc., with a concentrated potash solution; by the fermentation of crude tartaric acid by presence of lime; by distillation of oleic acid with nitric acid, in common with butyric, capronic, capric, pelargonic, and caprinic acid; by fermentation of glycerine; by distillation of caseine with dilute sulphuric acid and peroxide of manganese or chromate of potassa, simultaneously with formic, acetic, butyric, valerianic, and benzoic acid, oil, of bitter almonds, etc., and by the action of nitric acid upon oil of turpentine, etc.

*Oxyhydrate of Propionyl* (Oxyhydrate of Metacetyl):  $\text{HO,PrO}$ , is formed with many other products by the distillation of caseine, albumen, or fibrin with dilute sulphuric acid and peroxide of manganese or chromate of potassa. The distillate obtained is saturated with lime (which takes away the simultaneously formed acid), and then submitted to fractional distillation; what goes over between  $55$  and  $60^\circ$  is oxyhydrate of propionyl. Water-clear fluid of agreeable etheric odor, sp. gr.  $0.79$ ; in the air, in contact with platinum black, it is quickly converted into propionic acid.

Compounds  
of propionyl  
with oxygen.

*Propionic Acid* (Metacetic Acid):  $\text{HO,PrO}_2$ , is most easily obtained by boiling the nitropropionyl in a concentrated potassa solution so long as ammonia is evolved. We obtain propionate of potassa, which is decomposed by sulphuric acid. The pure hydrate crystallizes at a low temperature and boils at  $140^\circ$ ; tastes very acid; smells like butyric and acetic acid; is in large quantities soluble in water; if we add to the watery solution phosphoric acid or chloride of calcium, the propionic acid separates as an oily layer. —The *propionic acid salts* are soluble in water and possess the capability of crystallizing; the alkaline salts are unctuous to the touch. If the *ammonia salt* be distilled with anhydrous phosphoric acid, nitropropionyl is obtained.

*Propionamid*:  $\text{NH}_2, \text{PrO}_2$ , is obtained by bringing together aqueous ammonia and propionate of ethyl. The *silver salt* crystallizes in fine shining grains.

*Nitropropionyl* (Nitrometacetyl, Cyanethyl):  $\text{PrN}$ . With nitrogen. Forms by the action of cyanogen upon ethyl as well as by distillation of propionate of ammonia with anhydrous phosphoric acid. Colorless fluid of  $0.889$  sp. gr.; boils at  $180^\circ$ ; little

soluble in water. Boiled with solution of potassa, we obtain propionic acid accompanied by evolution of ammonia.

*Propion* (Metaceton):  $(C_4H_5, C_6H_5)O_2 = C_{10}H_{10}O_2$ . When a mixture of 1 part sugar with 8 parts quicklime is heated, an oily fluid passes over, which consists of acetone and propion, and can be separated by fractional distillation. Propion is a colorless fluid, insoluble in water, having an agreeable odor, boils at  $84^\circ$ , and treated with nitric acid, is converted into propionic acid; warmed with sulphuric acid and bichromate of potassa, acetic, propionic, and carbonic acid must be obtained. According to new investigations propion is a mixture of different bodies, consisting of an organic oxide:  $C_{12}H_9O$  with the oxyhydrates of the formyl series. The oxide thence contains a radical with the nucleus  $C_4 = (4C_2H_2, C_4H) = C_{12}H_9$ .

### THIRD MEMBER.

#### BUTYRYL.

a. Primary Radical:  $Bu = 3C_2H_2, C_2H = C_6H_7$ .

*Occurrence and Production.*—Butyryl is found as butyric acid in the fruit of *Ceratonia Siliqua*, in the old fruit of *Sapindus Saponariæ*, in *Tamarindus Indica*, often free in gastric juice, and in combination with oxide of glycyl in butter; it is produced by the fermentation of butyric acid, which always precedes the lactic acid fermentation; by the dry distillation of tobacco, by putridity of fibrine and caseine (in Limburg cheese it occurs with valerianic, capronic, capric acid, etc.), by heating fibrine with hydrate of potash, by distillation of the protein combinations with sulphuric acid and peroxide of manganese or chromate potassa, by decomposition of oleinic acid, by nitric acid (see Propionyl), etc.

*Oxyhydrate of Butyryl* (Butyral):  $HO, BuO$ , is obtained in addition to butyron by the dry distillation of butyrate of lime, or we distil the non-acid fluid obtained by the decomposition of fibrine, caseine, etc., by sulphuric acid and peroxide of manganese (*vide* Oxyhydrate of Propionyl); what goes over between  $70$  and  $100^\circ$  is collected by itself, and the intermingled oxyhydrate of propionyl is extracted by shaking with water. Water-clear, thin liquid, of penetrating smell and burning taste; boils at  $95^\circ$ ; sp. gr.  $0.821$ . Goes over in the air and under the co-operation of platinum quickly into butyric acid. Brought into contact with chlorine, at first we obtain bichlorbutyral,  $HO(C_2Cl_2, 2C_2H_2, C_2H)O$ , then quadri-chlorbutyral,  $HO(2C_2Cl_2, C_2H_2, C_2H)O$ . Besides, there is a compound known of bichlorbutyral with butyral. Bromine acts in the same way. Distilled with chloride of phosphorus, we obtain hydrochloric acid, phosphoric acid, and chlorbutyral,  $BuCl$ . Gives with ammonia a combination corresponding to aldehyd-ammonia; this compound crystallizes, and consists of  $NH_4O, BuO + 10aq$ .

*Hydrate of Butyric Acid* (Butyric Acid):  $HO, BuO$ . Butter,



from cow's milk is a mixture of butyrate, capronate, caprate, margarate, and oleate of glycy. If the butter be decomposed by aqueous potassa, glycerine is obtained, and a salt mixture of different acids; if it be distilled with water and sulphuric acid, the volatile acids, as butyric, capronic, caprinic, and capric acid, pass over with the aqueous vapor, whilst margaric and oleic acid remain behind; if the aqueous distillate be saturated with baryta, we can divide the different baryta salts by crystallization: first the salt of caprinic acid crystallizes, then that of capric acid, then that of capronic acid, and, finally, that of butyric acid. We obtain butyric acid in large quantities by means of fermentation. To a solution of sugar is added a small quantity of caseine, and so much carbonate of lime as is necessary for the saturation of the spontaneously forming butyric acid. The mixture is exposed to a steady temperature of  $30^{\circ}$ . The evolution of gas continues some weeks, and in the solution is found butyrate of lime, which is purified by re-crystallization; or, we set for a long time 4 pounds of ground *Siliquea dulcis*, with 10 pounds of water and 8 oz. chalk in a warm place of  $30$  to  $40^{\circ}$ , and stir from time to time; when the fermentation is ended, the butyrate of lime is separated, which is decomposed by sulphuric or hydrochloric acid. The pure butyric acid appears as a water-clear, thin-flowing fluid, of penetrating acid odor, like acetic acid and rancid butter, and biting acid taste; it leaves a white spot upon the tongue, and acts caustically upon the skin; soluble in all proportions in water, alcohol, and wood-spirit. From the aqueous solution it is separated by phosphoric acid as an oily layer; boils at  $164^{\circ}$ ; sp. gr. 0.976; burns with clear luminous flame; gives with *chlorine*, exposed to sunlight, bichlorobutyric and quadrichlorobutyric acid.

*Butyric Acid Salts*, in moist condition, smell like butter; they are soluble in water, crystallizable, and, when overflowed by sulphuric acid, evolve the penetrating odor of the acid. Most of the salts are mono-acid; with oxide of lead, it gives two combinations:  $3\text{PbO} + \text{BuO}_3$  &  $\text{PbO} + \text{BuO}_3$ . By shaking butyrate of methyl with aqueous ammonia, we obtain butyramid,  $\text{NH}_2\text{BuO}_2$ , as snow-white tables of a pearly lustre, which fuse at  $115^{\circ}$ , and, undecomposed, volatilize; is soluble in water, alcohol, and ether, and, distilled with chloride of phosphorus, gives nitrobutyryl. The same is also produced if butyrate of ammonia be distilled with anhydrous phosphoric acid.

*Protochloride of Butyryl* (Chlorbutyron):  $\text{BuCl}$ . We distil butyral with chloride of phosphorus. Colorless fluid, of peculiar odor and biting taste; boils at  $100^{\circ}$ ; lighter than water; soluble in the same; in all proportions miscible with alcohol and ether. Butyryl and chlorine.

*Nitrobutyryl* (Butyronitryl):  $\text{BuN}$ . Water-clear oil of agreeable odor; boils at  $118^{\circ}$ ; sp. gr. 0.795; by boiling in aqueous solution of potassa, gives ammonia Butyryl and nitrogen.



and butyrate of potassa; and, treated with potassium, gives cyanide of potassium, and, probably,  $C_6H_7$ .

b. *Derived Radicals.*

a. Bichlorbutyryl:  $C_2Cl_2, 2C_2H_2, C_2H = C_8H_5Cl_2$ .

β. Quadrichlorbutyryl:  $2C_2Cl_2, C_2H_2, C_2H = C_8H_3Cl_4$ .

*Oxyhydrate of Bichlorbutyryl* (Bichlorbutyral):  $HO, (C_8H_5Cl_2)O$ . If we let chlorine act in the sunlight upon butyryl during three hours, we obtain a neutral fluid which boils at  $200^\circ$ ; if the chlorine act in diffused daylight, we obtain a combination of butyral with bichlorbutyral  $= HO, C_8H_6ClO$ ; this is water-clear, boils at  $141^\circ$ , possesses a penetrating odor, gives no precipitate with  $AgO, NO_5$ .

*Bichlorbutyric Acid*:  $HO(C_8H_5Cl_2)O_3$ . Chlorine under co-operation of sunlight converts butyric acid, first into a tenacious, colorless fluid, of the above-given constitution; heavier than water, of peculiar odor.

*Oxyhydrate of Quadrichlorbutyryl* (Quadrichlorbutyral):  $HO(C_8H_3Cl_4)O$ , is obtained by farther action of chlorine upon bichlorbutyral. Thick, neutral, heavy oil, insoluble in water, soluble in alcohol, not volatile without decomposition.

*Quadrichlorbutyric Acid*:  $HO(C_8H_3Cl_4)O_3$ , is formed by the action of chlorine in the sunlight upon bichlorbutyric acid. Crystallizes from the etheric solution in oblique prisms, is insoluble in water, easily soluble in alcohol and ether, and appears to volatilize, unchanged, at  $140^\circ$ .

*Butyron*:  $(C_6H_7, ^\wedge C_8H_7)O_2 = C_{14}H_{14}O_2 = 4$  volumes Paired compounds of butyryl with butyl. Butyron. gas, is obtained in addition to butyral by cautiously heating butyrate of lime. The distillate is submitted to fractional distillation; at  $140$  to  $150^\circ$  pure butyron goes over. Colorless fluid, of peculiar, penetrating odor, and burning taste; is converted into a solid state by a mixture of solid carbonic acid and ether; scarcely soluble in water, easily soluble in alcohol and ether; boils at  $144^\circ$ , sp. gr. 0.83; burns with sooty flame; absorbs oxygen from the air with avidity. Gently warmed with ordinary dilute *nitric acid*, it forms propionic and butyric acid(?) Distilled with *chloride of phosphorus*, we obtain a compound  $= C_{14}H_{13}Cl$ , which presents a colorless, transparent fluid of penetrating odor, easily soluble in alcohol, and which swims upon water.

FOURTH MEMBER.

VALERYL.

a. Primary Radical:  $4C_2H_2, C_2H = C_{10}H_9 = Va$ .

Valeryl.

*Occurrence and Production*.—Valerianic acid is found in the root of the *Valeriana off.* and *Angelica*

off., in the berries and bark of *Viburnum opulus*, and in the oil of *Delphinus globiceps*.

By oxidation of amyl-spirit, we obtain valerianic acid, in the same manner as formic acid is obtained from wood-spirit; it arises from putrefaction of caseine (in Limburg cheese) by distillation of the proteine compounds with sulphate and chromate of potassa, by decomposition of oleic by nitric acid, by the action of potassa upon camomile oil, etc. etc.

*Oxyhydrate of Valeryl* (Valeral, Valeraldehyd):  $\text{HO}, \text{VaO}$ , is produced by dry distillation of valerianate of lime, simultaneously with valeron. A colorless, easily flowing fluid, of strong smell and burning taste, of 0.830 sp. gr.; boils at  $110^\circ$ ; insoluble in water, easily soluble in alcohol and ether; easily oxidizes, forming valerianic acid, and gives with *nitric acid* nitro-valerianic acid, but which is probably nitro-butyric acid.

Combinations  
of valeryl with  
oxygen.

*Hydrate of Valerianic Acid* (Valerianic Acid):  $\text{HO}, \text{VaO}_3$ . We distil a mixture of amyl-spirit, sulphuric acid, and chromate of potassa, with water, decompose with potassa the valerianate of amyl which passes over, and distil the obtained valerianate of potassa with sulphuric acid; or we distil dry valerian root with water, saturate the acid distillate with potassa, evaporate and decompose the residue with sulphuric acid. Valerianic acid appears as a colorless, oily fluid, of strong, acid, valerian-like odor, and suffocating, disagreeable, sharp, acid taste; brought upon the tongue, it leaves a white spot; soluble in all proportions in alcohol, ether, and acetic acid; it dissolves in 30 parts water, and takes up 20 per cent. of water; from the solution phosphoric acid precipitates it completely, with 2 atoms water =  $\text{HO}, \text{VaO}_3 + 2\text{aq}$ . The pure hydrate boils at  $175^\circ$ , and possesses a sp. gr. of 0.937; the combination with 2 atoms water boils at  $130^\circ$ . (Upon the decomposition of valerianate of potassium by the electric current, *v. Valyl*.) The *valerianic acid salts* all possess the peculiar sweetish odor of the acid; most of the salts are *uniacid*; however, a few basic and acid ones are known; some crystallize, others appear as a salty mass, without determined form. They are partly air proof, partly deliquescent, mostly soluble in water and alcohol. From the concentrated solution the valerianic acid itself is precipitated by acetic and succinic acids, as an oily acid,  $\text{HO}, \text{VaO}_3 + 2\text{aq}$ . Valerianic acid differs from the foregoing acids by its difficult solubility in water. Valerianic acid salts are obtained either direct or by double decomposition. The *ammonia salt* forms drusy needles, of sweetish taste and odor, and is completely volatile. If valerianate of ethyl be shaken with ammonia, thus we obtain *vale-ramid*,  $\text{NH}_2, \text{VaO}_2$ , and if the latter be distilled with anhydrous phosphoric acid, we thus obtain nitro-valeryl. The *potassa salt* crystallizes at  $32^\circ$ ; cauliflower-like, deliquescent, easily soluble in alcohol. The *baryta salt* crystallizes in transparent, shining,

easily pulverized prisms; readily soluble in water. The *zinc salt* crystallizes in spangle-like leaflets; soluble in alcohol and water; fuses at  $140^{\circ}$ , without losing acid.

The *Basic Lead Salt*:  $3\text{PbO} + \text{VaO}_3$ , appears in fine, shining needles, united in the form of bulbs, little soluble in water. The *Neutral Lead Salt*,  $\text{PbO}, \text{VaO}_3$ , forms shining leafy crystals, soluble in water, and becoming moist in the air. The *silver salt* separates from the hot aqueous solution in beautiful white leaflets, which quickly become black in the light.

*Acetate of Oxychloride of Valeryl*:  $\text{Va} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right. + \text{AcO}_3$ , is obtained by the introduction of chlorine into acetate of amyl. Colorless, rather mobile fluid, agreeable odor; insoluble in water, easily soluble in alcohol and ether, heavier than water, not volatile.

*Nitrovaleryl*:  $\text{VaN}$ . Oily fluid of disagreeable odor, like oil of bitter-almonds; boils at  $118^{\circ}$ ; sp. gr. 0.795. Boiled with potassa, we obtain valerianic acid and ammonia; is also obtained by decomposition of fibrin with sulphuric acid and chromate of potassa.

#### b. Derived Radicals.

a. Bichlor-valeryl:  $\text{C}_2\text{Cl}_2, 3\text{C}_2\text{H}_2, \text{C}_2\text{H} = \text{C}_{10}\text{H}_7\text{Cl}_2$ .

β. Quadrichlor-valeryl:  $2\text{C}_2\text{Cl}_2, 2\text{C}_2\text{H}_2, \text{C}_2\text{H} = \text{C}_{10}\text{H}_5\text{Cl}_4$ .

γ. Hexachlor-valeryl:  $3\text{C}_2\text{Cl}_2, \text{C}_2\text{H}_2, \text{C}_2\text{H} = \text{C}_{10}\text{H}_3\text{Cl}_6$ .

*Bichlor-valerianic Acid*:  $\text{HO}(\text{C}_{10}\text{H}_7\text{Cl}_2)\text{O}_3$ . Chlorine gas is conducted into the hydrate of valerianic acid in diffused day light, and in the beginning the acid strongly refrigerated. Semi-fluid, transparent, heavy, inodorous, of sharp, burning taste, leaving upon the tongue a white spot. Forms with water a very fluid, almost inodorous compound. Unites with bases to form salts.

*Quadrichlor-valerianic Acid*:  $\text{HO}(\text{C}_{10}\text{H}_5\text{Cl}_4)\text{O}_3$ . If bichlor-valerianic acid be exposed to the action of chlorine in the sunlight, we obtain the quadrichlor-valerianic acid. Semi-transparent, inodorous, of sharp, burning, somewhat bitter taste, rather easily soluble in water; if the acid be precipitated by a stronger acid from the ammonia salt, it appears oily, and consists of  $\text{HO}(\text{C}_{10}\text{H}_5\text{Cl}_4)\text{O}_3 + 2\text{aq}$ . This acid, which contains water, decomposes after a little time under production of hydrochloric acid; non-volatile. The *potassa salt* quite equals the valerianate of potassa; all the salts are not easily soluble in water, or are insoluble. The *silver salt* decomposes after a little time under the production of chloride of silver.

*Terchloride of Hexachlor-valeryl*:  $(\text{C}_{10}\text{H}_3\text{Cl}_6)\text{Cl}_3$ , is obtained, if chloride of amyl be exposed to the action of chlorine in the sunlight (*vide* Chloride of Amyl).

*Valeron*:  $(C_8H_9, C_{10}H_9)O_2 = C_{18}H_{18}O_2$ , arises by distillation of valerianate of lime, with valeral. Colorless fluid; boils at  $180^\circ$ . Paired compounds of valeryl. Valeron.

## FIFTH MEMBER.

## CAPRONYL.

a. Primary Radical:  $5C_2H_2, C_4H = C_{12}H_{11} = Ca$ .

*Occurrence and Production*.—Capronyl is found in butter, and in cocoa-nut oil, in common with capric, capronic, and laurostearinic acid. If cyanogen act upon amyl, nitro-capronyl is obtained; it farther arises by the action of nitric acid upon oxyhydrate of oenanthyl, as well as by decomposition of fibrin by sulphuric acid and chromate of potassa. Also we obtain capronic acid, if rape-seed oil be distilled, and the distillate oxidized by nitric acid, simultaneously with acetic, propionic, butyric, valerianic, and oenanthylic acid (compare also butyryl and propionyl). Capronyl.

*Hydrate of Capronic Acid*:  $HO, CaO_3$ . Cocoa-nut oil is boiled a few hours with a concentrated soda solution, and afterwards we distil the mass decomposed with sulphuric acid. The acid distillate is saturated with baryta, and evaporated; we obtain at first crystals of caprinat and caprate of baryta; and, at last, the capronate of baryta crystallizes, from which the capronic acid is precipitated by dilute sulphuric acid. In the same manner it can be procured from butter and Limburg cheese. If nitro-capronyl be boiled with an aqueous potassa solution, we obtain capronate of potassa and ammonia; water-clear, oily fluid of peculiar odor, like perspiration, and a strongly sour, afterward sweetish taste, like nitric ether; it dissolves in 96 parts water, and mixes with alcohol in all proportions; sp. gr. 0.930; boiling point  $198$  to  $202^\circ$ . Combinations of capronyl.

The *capronic acid salts* agree with the valerianic, only they are less soluble in water. (Upon the decomposition of capronate of potassa, by the electric current, see *Amyl*.)

*Nitrocapronyl* (Cyanamyl):  $CaN$ , arises by the action of cyanogen upon amyl, and is obtained by the distillation of amyl-sulphate of potassa with cyanide of potassium. Mobile liquid, of peculiar odor; little soluble in water, easily soluble in alcohol; sp. gr. 0.806; boiling point  $146^\circ$ . Capronyl and nitro-

*Capron* (Oxide of Amyl-capronyl):  $(C_{10}H_{11}, C_{12}H_{11})O_2 = C_{22}H_{22}O_2$ , is formed by dry distillation of capronate of baryta simultaneously with propylen gas; the crude distillate obtained is purified by repeated rectification. Colorless fluid, of peculiar odor; insoluble in water, soluble in alcohol and ether; becomes in the air of a brown color; boils at  $165^\circ$ ; lighter than water. Treated with nitric acid, capron leaves a compound, which must consist of  $(C_{10}H_8NO_4)O_3$ ; this body is therefore nitro-valeric acid. Paired combinations of capronyl. Capron.



## SIXTH MEMBER.

## OENANTHYL.

a. Primary Radical:  $6C_2H_2, C_2H=C_{14}H_{13}=Oe$ .

*Production*.—Oenanthyl is formed by the action of nitric acid upon ricinus oil, oleinic and margaric acid, wax, as well as by dry distillation of ricinus oil (ricinus oil consists of palmitate and ricinate of glycy).

*Oxyhydrate of Oenanthyl* (Oenanthol):  $HO, OeO$ , is found among the products of distillation of ricinus oil. Water-clear fluid, which boils at  $155^\circ$ . If oenanth oil be treated with concentrated potassa solution, it separates into oenanthic acid, *hydraoenanthyl*,  $C_{14}H_{13}H$ , which goes over by distillation. This body is colorless, of slight citron odor, boils at  $220^\circ$ ; little soluble in water, easily soluble in alcohol and ether; burns with a clear flame, and, by heating with nitric acid, gives oenanthic acid. *Chlorine* decomposes oenanth oil. If the oil be permitted to fall in drops into strong *Nitric Acid*, a violent reaction takes place, under production of capronic and oenanthic acid, and a peculiar compound which also arises by the action of nitric acid upon choloidic acid, and is named *Nitracol*. This body precipitates again, if the mass be distilled, and the distillate mixed with water; it is colorless, and of a penetrating, exciting odor; decomposes by boiling with water into nitrous acid and *Chloracrol*,  $C_8H_5N_2O_{13}$ , which gives with potassa, under separation of an oil, a salt consisting of  $KO, C_2HNO_9$ . Oenanthyl combines with ammonia; and if into the aqueous solution sulphurous acid be conducted, we obtain a white crystalline powder, which consists of  $NH_4O + C_{14}H_{13}O + 2SO_2$ .

*Hydrate of Oenanthic Acid*:  $HO, OeO_3$ . Ricinus oil is gently warmed in a retort, with twofold weight of moderately concentrated nitric acid; a powerful reaction soon commences, at the termination of which there is found in the retort a fatty body, and a watery fluid. The latter is distilled with much water. The oily acid which goes over with the water is removed, and purified by repeated distillation with water. Completely colorless, transparent fluid, insoluble in water, of peculiar aromatic odor, and suffocating, exciting taste; only distillable with water, without decomposition. The *copper salt* crystallizes in beautiful green needles, of silken lustre; the *silver salt* submitted to distillation gives a body not acid, and crystallizing in needles. By *Electrification*, the *potassa salt* gives a combination  $C_{12}H_{13}$ .

b. *Derived Radicals*.

$\alpha$ . Bichloroenanthyl:  $C_2Cl_2, 5C_2H_2, C_2H=C_{14}H_{11}Cl_2$ .

$\beta$ . Quadrichloroenanthyl:  $2C_2Cl, 4C_2H_2, C_2H=C_{14}H_9Cl_4$ .

*Oxyhydrate of Bichloroentanhyll*:  $\text{HO}(\text{C}_{14}\text{H}_{11}\text{Cl}_2)\text{O}$ , is obtained by the introduction of chlorine into oenanthol. If the decomposition goes farther, we obtain a compound of oxyhydrate of bichloroentanhyll with oxyhydrate of quadrichloroentanhyll, which appears like a thin-flowing oil.

*Oenanthic Acid* ( $\text{C}_{14}\text{H}_{13}\text{O}_2$ ). In wine-fuselole, a peculiar acid is found, in combination with oxide of ethyl, which the odor of the acid determines, and is named oenanthic acid. The same acid is found in fuselole of grain-whiskey; it contains one atom less of oxygen than oenanthic acid; but it seems not to be converted into the latter by oxidation. We obtain the acid as an hydrate, if wine-fuselole be boiled with potassa solution, and the obtained potassa salt decomposed by sulphuric acid. The acid separates in the form of a colorless and inodorous oil, which contains 2 atoms water; if the alcoholic solution be quickly evaporated, we obtain a hydrate as a white butter-like mass, which melts at  $13^\circ$ ; is inodorous and tasteless; insoluble in water, easily soluble in alcohol and ether. If the hydrate be submitted to distillation, later anhydrous acid goes over; it is solid, melts at  $31^\circ$ , and volatilizes at  $295^\circ$ ; by repeated sublimation, it is said to be converted into margaric acid; a weak acid, which only with difficulty forms permanent salts. If Chlorine be conducted into pure fuselole, we obtain *Chloroentanthat* of *Oxychloride* of *Chloracetyl*  $= (\text{C}_4\text{Cl}_3) \left\{ \begin{array}{c} \text{O} \\ \text{Cl}_2 \end{array} \right.$ , combined with  $(\text{C}_2\text{Cl}_2, \text{C}_{12}\text{H}_{11})\text{O}_2$ , as a colorless, syrup-thick, non-volatile fluid, of agreeable odor, and bitter, offensive taste. Brought together with potassa, we obtain acetate(?) and bichloroentanthat of potassa, beside chloride of potassium.

*Hydrate of Capric (Caprylic) Acid*:  $\text{HO}, \text{CpO}_3$ , is found in butter and cocoa-nut oil; likewise in old cheese (compare also butyric and capronic acid). We obtain the capric acid by decomposition of the baryta salt; its production has been given at butyric and capronic acid. Colorless, below  $13^\circ$  solid, of slight, not agreeable odor; scarcely soluble in water, but easily soluble in alcohol, and ether; sp. gr. of the fused acid = 0.911; boiling point  $236^\circ$ . The *baryta salt* crystallizes in fine scales of a fatty lustre; decomposes by dry distillation into carbonic acid, and *Caprylon*  $(\text{C}_{14}\text{H}_{15} + \text{C}_{16}\text{H}_{15})\text{O}_2 = \text{C}_{30}\text{H}_{30}\text{O}_2$ .

*Hydrate of Pelargonic Acid*:  $\text{HO}, \text{PgO}_3$ . This acid is found in *Pelargonium roseum*; it is formed by oxidation of oleic acid by nitric acid, as well as by the action of nitric acid upon rue-oil simultaneously with caprinic acid. the acid fluid, which goes over in the oxidation of oleic acid, be saturated with baryta, we obtain by evaporation, at first, crystals of capronate, then of pelargonate, and, at last, of caprinate of baryta. The pelargonate of baryta,

Appendix to  
oenanthyl.

7th Member.  
Capryl:

$\text{Cp. } 7\text{C}_2\text{H}_2, \text{C}_2\text{H}$   
 $= \text{C}_{16}\text{H}_{15}$ .

8th Member.

Pelargonyl: Pg.

$8\text{C}_2\text{H}_2, \text{C}_2\text{H} =$   
 $\text{C}_{18}\text{H}_{17}$ .

which crystallizes in large leaves, is decomposed by sulphuric acid. An oily, greasy acid, which easily becomes solid, scarcely soluble in water, but easily soluble in alcohol and ether.

## NINTH MEMBER.

## CAPRINYL.

Primary Radical:  $9C_2H_2, C_2H=C_{20}H_{19}=Cr.$

*Occurrence and Production.*—Rue-oil is probably oxyhydrate of caprinyl. Caprinic acid is found in butter, in train-oil from the *Faroer*, in old cheese; it is formed in the oxidation of oleic acid by nitric acid, etc.

*Oxyhydrate of Caprinyl* (Rue-oil):  $HO, CrO$ . Rue-oil, which is procured by distillation of *Ruta graveolens*, and also by heating a mixture of cod-liver oil with sulphuric acid, is distilled, and the last third, which goes over, received by itself. A colorless oil, which at  $-2^\circ$  forms shining crystals, boils at  $236^\circ$ , and possesses a specific gravity  $=0.831$ . If, in the form of vapor, it be conducted over chloride of zinc, it decomposes, forming a hydrocarbon. If hydrochloric acid gas be conducted into the alcoholic solution, it is converted into a metamerie compound, which, after a little time, crystallizes, and possesses an agreeable odor, like fruit; if rue-oil be heated with an equal quantity of moderately concentrated nitric acid, a violent reaction takes place, at the end of which pelargonic and caprinic acid (*Rutin-saure*) are found in the acid fluid.

*Hydrate of Caprinic Acid* (Caprinic Acid):  $HO, CrO_3$ , is obtained by decomposition of the baryta salt, which is procured simultaneously with pelargonate, capronate, caprinic acid of baryta, etc. (*v.* these acids). Crystallizes in fine needles, melts at  $18^\circ$ , possesses an odor like perspiration, and a strong acid taste, afterwards sweet; requires 1000 parts water for solution; mixes with alcohol in all proportions. If the hydrate be treated with chloride of phosphorus, we obtain oxychloride of capronyl,  $(C_{20}H_{19}) \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right.$ , which, brought in contact with potassa, decomposes in caprinic acid under formation of chloride of potassium.

*Caprinic acid of Baryta* crystallizes in fine needles of a fatty lustre, and by spontaneous evaporation in fine scales.

*Hydrate of Cocylic Acid* (Cocinic Acid):  $HO, CO_3$ , is obtained by saponification of cocoa-nut oil with potassa; the obtained soap is decomposed by an acid, and the volatile acids removed by distillation. The cocylic acid remains behind, and is purified by recrystallization. Crystallizes in needles, uniting in stelliform groups; is colorless and inodorous; fuses at  $35^\circ$ , and stiffens to a crystalline mass. By distillation of the lime-salt, the cocinon  $C_{42}H_{42}O_2$  must be obtained. According to other accounts, cocinic acid consists of

10th Member.

Cocyl:

$Co. 10C_2H_2, C_2H$   
 $=C_{22}H_{21}$

$C_{26}H_{52}O_2$ ; also, cocinic acid is affirmed to be a mixture of laurostearic and caprinic acids; the principal ingredient of cocoa-nut oil must be laurostearic acid, with a small addition of palmitic and myristic acids.

*Laurostearic Acid*:  $HO, LaO_3$ , is found in laurel-berry fat, in pichurim beans, and in cocoa-nut oil, in combination with Oxide of Glycyl. We saponify laurel-berry fat, and precipitate the acid with tartaric acid, and purify it by recrystallization from the alcoholic solution. Snow-white needles of silky lustre, melts at  $43^\circ$ , easily soluble in alcohol and ether; from the alcoholic solution the *soda salt* is obtained in indistinct crystals.

*Hydrate of Myristic Acid*:  $HO, MyO_3$ , is found in the fat of the *Myristica moschata*. Muscat-butter is extracted by ordinary alcohol, which leaves behind myristate of Glycyl and Myristicin, from which the acid is obtained in the same manner, as laurostearic acid from laurel-berry fat. Easily soluble in boiling alcohol, from which, after cooling, it is deposited mostly crystalline, snow-white; melts at  $49^\circ$ ; the *potassa salt* is white, crystalline, and soluble in alcohol and water.

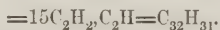
*Hydrate of Behylic Acid* (Behenic Acid), is found in behen-oil, which is procured from *Moringa aptera*, with margaric and moringic acids. Crystallizes from the alcoholic solution in large warts, which fuse at  $52^\circ$  (compare behenylic acid).

10th Member.  
Laurostearyl:  
 $La. 11C_2H_2, C_2H$   
 $=C_{24}H_{23}$ .

13th Member.  
Myristicyl:  
 $My. 13C_2H_2, C_2$   
 $H=C_{28}H_{27}$ .

14th Member.  
Behyl:  $By. 14C_2$   
 $H_2, C_2H=C_{30}$   
 $H_{29}$ .

#### FIFTEENTH MEMBER.



#### PALMITIC, ETHALIC, OLIDIC, MADIAC, AND BOGBUTYRIC ACID.

The above-named acids all correspond to the formula  $HO, C_{32}H_{64}O_2$ , also their properties agree in the essentials. They differ only in their melting point, which in palmitic and olidic acids lies at  $60$  to  $70^\circ$ ; in ethalic, madiac, and bogbutyric acids, at  $54^\circ$ ; it is yet to be investigated whether these differences do not rest upon errors of observation.

*Hydrate of Palmytic Acid*, is found in palm oil, which is derived from the *Avvira Elais*, also in Japanese wax, beeswax, cocoanut oil, and ricinus oil. From palm oil, particularly from the old, the palmitic acid is obtained in the same manner as laurostearic acid is from laurel-berry fat. It crystallizes in completely white needles, which unite in the form of tufts, and may be distilled without decomposition. Chlorine decomposes the acid, forming derived acids; the compound containing the most chlorine consists of  $(4C Cl_2 11 C_2H_2, C_2H)O_3$ . All the acids unite with bases; we obtain the *soda salt* crystalline.



*Hydrate of Ethalic Acid.* This acid behaves towards ethal (oxyhydrate of cethyl) as acetic acid towards alcohol. If ethal be heated with hydrate of potassa, ethalate of potassa is obtained, accompanied by evolution of hydrogen gas. Purified spermaceti is ethalate of cethyl. One part spermaceti and one-half part hydrate of potassa are fused together at  $110^{\circ}$ ; and the obtained mass, ethalate of potassa, extracted by boiling water; hydrochloric acid precipitates the ethalic acid. To obtain it pure, it must be repeatedly treated with hydrate of potassa. Crystallizes from the alcoholic solution in needles, united in the form of moss; colorless and inodorous, insoluble in water, but soluble in boiling alcohol and ether. Volatilizes undecomposed.

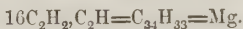
*Olidic Acid* is obtained, if oleic acid be heated with a great excess of hydrate of potassa, until hydrogen is evolved. The mass is brought into water, the olidate of potassa which separates is removed, and from its aqueous solution the acid procured; a crystalline, pulverizable, snow-white mass.

*Madic Acid* is obtained from Madia oil (from *Madia Sativa*). Crystallizes from the alcoholic solution in radiated groups of fine needles.

*Bogbutyric Acid.* In the turf-moors of Ireland is found the so-called bog-butter; it is easily pulverizable, whitish, and easily soluble in hot alcohol; the solution stiffens after cooling to a mass of fine needles; reacts acid.

## SIXTEENTH MEMBER.

## MARGARYL.



*Occurrence.*—Most fats found in the vegetable and the animal kingdom are mixtures of margarate, stearate, and oleate of glyceryl. If the generally diffused fats be treated with pure alkalies, we obtain a salt mixture of the acids mentioned, which mixture is commonly called *soap*. If by an acid a solution of the soap be decomposed, the fatty acids are deposited. Margaric and stearic acid are solid, the oleic acid is fluid at common temperatures. The hydrate of margaric acid consists of  $HO(C_{34}H_{33})O_3$ , and that of stearic acid of  $2HO + (2C_{34}H_{33})O_5$ . Hence, if we denote  $C_{34}H_{33}$  as margaryl: Mg, margaric acid is  $HO, MgO_3$ , and stearic  $2HO, Mg_2O_5$ . The correctness of this view is corroborated by the immediate conversion of stearic acid into margaric acid by oxidizing bodies.

*Hydrate of Margaric Acid:*  $HO, MgO_3$ . Margaric acid is found most abundantly in human fat, hogs' lard, mutton tallow, and beef's tallow, olive oil, linseed oil, butter, the substance of the brain, the so-named Shea-butter, Chinese tallow (from *Stillingia sebifera*); it is formed by distillation, and oxidation of stearic acid, etc. It is best produced from olive oil or human fat. These are saponified

Combinations  
of margaryl  
and oxygen.

with potassa, and the aqueous solution is decomposed with acetate of lead. The precipitate, consisting of margarate and oleate of lead, is dried, and then several times extracted with boiling ether, which dissolves the oleate of lead. The margarate of lead remaining behind is decomposed by an acid, and the precipitated margaric acid obtained by crystallization from the alcoholic solution. From the hot, saturated alcoholic solution margaric acid crystallizes, during the cooling, in white, shining, tasteless, and inodorous scales, which melt at  $60^{\circ}$ ; the fused acid stiffens in white, shining prisms passing through each other; insoluble in water, not easily soluble in cold alcohol, but easily soluble in hot alcohol and in ether; distils without decomposition, and burns with a clear flame; sp. gr. 0.844. If margaric acid be a long time boiled with nitric acid, it is by degrees decomposed, under formation of suberic, pimilic, lipinic, adipinic, and succinic acids. Fused together with *anhydrous phosphoric acid*, over the water bath, we obtain jelly-like lumps, which fuse at  $60$  to  $65^{\circ}$ .

*Margaric Acid Salts.* Margaric acid is weak; it dissolves, in the cold, in a solution of carbonate of potassa under production of bicarbonic acid salt; at  $100^{\circ}$  it expels the carbonic acid. It forms basic, neutral, and acid salts, only the prot-acid compounds with the pure alkalies are soluble in water; if common salt, or potash-lye, be added to the solution, the compounds again separate. If the concentrated aqueous solution of the neutral alkali salts are mixed with 1000 parts water, they are thus decomposed into double-acid salts, which are deposited, whilst free potassa is separated; by repeated treatment with much water, these salts are converted into ter-acid and quadri-acid salts. *Margarate of ammonia* crystallizes in small scales of an acid salt, having a mother-of-pearl lustre. If ammonia gas be conducted into an alcoholic solution of olive-oil, we obtain a soap-like mass; if this be treated with boiling water, there separates upon the surface *Margaramid*  $\text{NH}_2$ ,  $\text{MgO}_2$ , which crystallizes in needles from the alcoholic solution.

*Margarate of Potassa:*  $\text{KO}, \text{MgO}_3$ , is obtained, in shining scales, by evaporation of the alcoholic solution. One part salt with 10 parts water, forms, at  $12^{\circ}$ , a cloudy slime, which becomes completely transparent at  $70^{\circ}$ ; it requires for solution 6 parts boiling alcohol; the solution continues after the cooling.

*Bimargarate of Potassa:*  $\text{KO}, \text{HO}, 2\text{MgO}_3$ , is obtained, if the prot-acid salt be dissolved in 24 parts boiling water, and the solution be poured in 1000 parts cold water; it separates leaflets of a mother-of-pearl lustre. If the bi-acid salt be treated with water, it reacts alkaline, under production of ter-acid and quadri-acid combinations, which are deposited. If the biacid-salt be brought together with 1000 parts warm water, there arises a milky fluid, from which, after cooling to  $26^{\circ}$ , scales separate of a mother-of-pearl lustre, consisting of bi-acid and ter-acid salts. If this precipitate be again boiled with 1000 parts water, a quadri-acid salt

is formed, which, during the cooking, becomes a white swollen mass; boiling alcohol divides the ter-acid salt into bi-acid and hydrate of margaric acid.

*Margarate of Soda*:  $\text{NaO}, \text{MgO}_3$ , is a salt, easily soluble in alcohol; and which forms, with a little water, a stiff jelly-like soap, which becomes solid by cooling; it decomposes, in contact with water, like the potassa salt. The *baryta salt*,  $\text{BaMgO}_3$ , appears as a white powder, insoluble in water; likewise the lime-salt.

*Margarate of Lead*:  $\text{PbO}, \text{MgO}_3$ . If a solution of acetate of lead be added to an alcoholic solution of the neutral soda-salt, a voluminous precipitate is formed, which is heavier after drying, and which melts by heating to a doughy, plaster-like, transparent mass. If the neutral lead-salt be digested, a few days, with vinegar of lead, we obtain a granular mass, no longer fusible, and which consists of  $2(\text{PbO}, \text{MgO}_3) + (6\text{PbO} + \text{AcO}_3)$ .

*Hydrate of Stearic Acid*:  $2\text{HO} + \text{Mg}_2\text{O}_5$ , is found most abundantly in animal and vegetable tallow. Tallow-soap (best from mutton tallow) is dissolved in 6 parts boiling water; the solution decomposed by hydro-chloric acid, and the deposited mixture of stearic and oleic acids pressed between warmed metal-plates so long as oleic acid still flows out; what remains behind, is impure stearic acid, and serves for stearine candles. By repeated crystallization from boiling alcohol, we obtain the pure acid; if its melting point lies below  $70^\circ$ , margaric acid is admixed. From the hot alcoholic solution, the stearic acid crystallizes at  $50^\circ$  in large shining scales; insoluble in water, with boiling alcohol miscible in all proportions; after cooling, the concentrated solution stiffens; also soluble in boiling ether; the alcoholic solution reacts slightly acid. Stearic acid burns with a clear flame; specific gravity of the fused acid equals 0.854. If it be heated a short time with concentrated *nitric acid*, or with sulphuric and chromic acid, it is converted into margaric acid. By the farther action of nitric acid, we obtain the products mentioned in connection with margaric acid.

*Stearic Acid Salts*. They resemble those of margaric acid. The neutral alkali salts are soluble in water, and, by treatment with much water, are converted into free alkalies, and acid salts; the compounds with the alkaline earths, the earths, and the oxides, of the heavy metals, are insoluble; they are most easily obtained by double decomposition. The neutral salts correspond to the formulæ  $2\text{BO} + \text{Mg}_2\text{O}_5$ , and  $\text{BO}, \text{HO}, \text{Mg}_2\text{O}_5$ .

The *Potassa Salt*,  $2\text{KO} + \text{Mg}_2\text{O}_5$ , crystallizes from the hot alcoholic solution, in white, fatty, infusible, shining scales. One part salt forms, with 10 parts cold water, an opaque slime, which melts at  $99^\circ$ , and stiffens, after the cooling, to a shining mass; dissolves in 25 parts boiling alcohol; the solution stiffens after cooling. If the neutral salt be dissolved in 100 parts hot water, during the cooling there separates, under the liberation of pure potassa, a mixture, which consists of  $(2\text{KO} + \text{Mg}_2\text{O}_5) + (\text{KO}, \text{HO}, \text{Mg}_2\text{O}_5)$ . The



compound  $\text{KO}, \text{HO}, \text{Mg}_2\text{O}_5$  is also obtained, if 1 part  $2\text{KO} + \text{Mg}_2\text{O}_5$  be dissolved in 20 parts boiling water, and the solution mixed with 1000 parts water; crystallizes from the alcoholic solution in leaflets of a mother-of-pearl lustre, which are soft at  $100^\circ$ . If this salt be repeatedly treated with 1000 parts of boiling water, a turbid, milky fluid arises, which, at  $75^\circ$ , is transparent and mobile, and which deposits, at  $67^\circ$ , leaflets of mother-of-pearl lustre, consisting of  $\text{KO}, 3\text{HO} + 2\text{Mg}_2\text{O}_5$ ;  $3(\text{KO}, \text{HO}, \text{Mg}_2\text{O}_5) = (2\text{KO} + \text{Mg}_2\text{O}_5) + (\text{KO}, 3\text{HO} + 2\text{Mg}_2\text{O}_5)$ .

The *Soda Salt*,  $2\text{NaO} + \text{Mg}_2\text{O}_5$ , behaves like the potassa salt.

The *Stearate of Lead*,  $2\text{PbO} + \text{Mg}_2\text{O}_5$ , appears as a white, fusible mass, insoluble in water. If we melt together 21 parts of oxide of lead and 100 parts of stearic acid, we obtain a solid, gray-white mass of radiated fracture, which melts at  $100^\circ$ , slightly soluble in boiling alcohol, and consists of  $\text{PbO}, \text{HO}, \text{Mg}_2\text{O}_5$ . If stearic acid be boiled with vinegar of lead under exclusion of air, we obtain a hard, transparent mass, which consists of  $4\text{PbO} + \text{Mg}_2\text{O}_5$ .

*Margarin-sulphuric Acid*. If olive-oil be mixed with half its weight of sulphuric acid in small quantities, a slightly colored pasty mass is thus obtained, which consists of paired compounds of margaric acid, oleic acid, and glycerine with sulphuric acid; free sulphuric acid is also obtained. If the mass be mixed with threefold its weight of warm water, there are deposited margarin-sulphuric, and olein-sulphuric acid, in the state of syrup, and can be easily removed. The separation of both acids is impossible; they both dissolve in alcohol and water. If the watery solution be left standing a little time, meta-margaric and meta-oleinic acid are deposited, and in the solution is found sulphuric acid in combination with hydro-margaritinic acid; if this solution be warmed, the hydro-margaritin-sulphuric acid decomposes into hydro-margaritinic and sulphuric acid, the former of which is deposited. But if an aqueous solution of margarin-sulphuric and olein-sulphuric acid be immediately heated, before the separation of the meta-margaric acid takes place, hydro-margaric acid is obtained, simultaneously with hydro-oleinic acid, both of which are deposited, and the solution contains pure sulphuric acid. Meta-margaric and hydro-margaric acid are solid, and can be separated by expression from the fluid meta-oleinic and hydro-oleinic acid. The following formulæ appear to represent these combinations:—

Metamargaric Acid	$\text{HO}(\text{C}_{34}\text{H}_{33})\text{O}_3$ .
Hydromargaric Acid	$\text{HO}(\text{C}_{34}\text{H}_{34})\text{O}_4$ .
Hydromargaritic Acid	$\text{HO}(\text{C}_{34}\text{H}_{35})\text{O}_5$ .

Metamargaric acid melts at  $50^\circ$ , the hydromargaric at  $70^\circ$ , and the hydromargaritic at  $68^\circ$ .



Margaron.

*Margaron*:  $(C_{32}H_{33}, \neg C_{34}H_{33})O_2 = C_{65}H_{65}O_2(?)$ . If a mixture of margaric acid with quicklime be distilled, margaron is obtained—a mass, fusible at  $76^\circ$ , and of a mother-of-pearl lustre.

*Stearophanic Acid*. In the seeds of the *Cocculus* 17th Member.  
Stearophanyl: *Indicus* (semina cocculi indici) there is found in combination with oxide of glycyll, an acid, which fuses at  $68^\circ$ , and is named stearophanic acid. An acid of the same constitution,  $HO, C_{36}H_{35}O_3$ , is found in bassia oil (from *Bassia latifolia*) in common with palmitic acid; it melts at  $70^\circ$ , but agrees in the remaining properties with stearophanic acid. The coccle seed, freed from the white shell, is extracted with boiling alcohol, and the fat, which separates during cooling, is purified by repeated crystallization from boiling alcohol. The pure fat is saponified with potash, and the acid obtained from the soap, in the ordinary way. Crystallizes in small needles of mother-of-pearl lustre; the fused acid, by cooling, stiffens in star-formed groups. Easily pulverized, readily soluble in pure alcohol, and completely separates after cooling; gives, with soda, a crystallizable salt; in other respects, the salts behave like the margaric acid-salts. The acid procured from the bassia-oil, and purified by repeated crystallization from ether, is converted, by the action of chlorine, into deca-chlor-bassiaic acid  $= HO(5C_2Cl_2, 12C_2H_2, C_2H)O_3$ .

21st Member.

Behynyl:

Bh.  $21C_2H_2, C_2$   
H  $= C_{44}H_{43}$

*Behynylic Acid*:  $HO, BhO_3$ , is found in behen-oil, which is procured from the nut of *Moringa oleifera*. It is a mixture of oleate, margarinate, and behenate, of glycyll. The behen-oil soap is decomposed by hydrochloric acid, the acid mixture repeatedly dissolved in alcohol, and the crystals, which are first deposited, collected. The behenic acid is pure, if the melting point lies at  $76^\circ$ ; it stiffens in white, shining crystals, which are very friable, and agree in the remaining properties with stearic acid.

### The Wax Acids.

23d Member.

Cerosyl:

Cy.  $23C_2H_2, C_2$   
 $= C_{48}H_{47}$

*Cerossic Acid*,  $HO, CyO_3$ . An intimate mixture of cerossin (sugar-cane wax) and potassa-lime, is heated in a metal-bath to  $250^\circ$ . Accompanied by evolution of hydrogen, cerosinate of potassa is formed, which is decomposed by boiling with water and hydrochloric acid. From the hot solution in naphtha, the acid crystallizes during the cooling; it is white, fuses at  $93^\circ.5$ , and is only slightly soluble in alcohol and boiling ether.

26th Member.

Ceretyl: Ct.26

$C_2H_2, C_2H = C_{54}$   
H  $= C_{53}$

*Cerotic Acid* (Cerin):  $HIO, CtO_3$ . Beeswax consists essentially of cerotic acid and miricin. If the wax be boiled with alcohol, the cerotinic acid is precipitated during the cooling. The acid is saponified

with caustic potassa, and the soap decomposed by an acid. From the separated acid the baryta salt is produced; the latter after drying is repeatedly extracted with ether, and the acid separated by hydrochloric acid. It is also obtained by heating cerotin (p. 116) with hydrate of potassa. From the boiling alcoholic solution we obtain the cerotic acid in crystals; it melts at  $79^{\circ}$ ; is converted by the action of chlorine into  $\text{HO}(6\text{C}_2\text{Cl}_2, 21\text{C}_2\text{H}_2, \text{C}_2\text{H})\text{O}_3$ . From the Ceylon beeswax the acid cannot be obtained.

*Melissic Acid:*  $\text{HO}, \text{MyO}_3$ . Melissin (oxyhydrate of melissyl) is fused with potassa lime; accompanied by evolution of hydrogen, there is produced melissic acid, whose particular properties are not known.

29th Member.  
Melissinyl:  
 $\text{My}, 29\text{C}_2\text{H}_2, \text{C}_2$   
 $\text{H} = \text{C}_{60}\text{H}_{39}$ .

*Salt-like Combinations of the Oxides of the Methyl Group with the Acids of the Formyl Group.*

As the oxides of the methyl group combine with inorganic acids, so also do they with organic acids. The production of these combinations is given in general, on p. 94.

Combinations  
of the oxide of  
methyl.

*Formate of Methyl:*  $\text{MeO}, \text{FoO}_3$ . Colorless, etheric fluid; boils at  $34^{\circ}$ ; sp. gr. 0.9447. By action of chlorine is converted first into formate of oxychloride of formyl, and at last into chlorformate of oxychloride of chlorformyl.

*Basic Formate of Methyl (Formal):*  $3\text{MeO} + \text{FoO}_3$  or  $\text{HO}, \text{MeO}, (\text{C}_2\text{H})\text{O}$ . Two parts wood-spirit, two parts peroxide of manganese, and two parts sulphuric acid, mixed with an equal portion of water, are submitted to gentle distillation. The distillate is rectified, and what passes over at  $40^{\circ}$  is collected alone. Colorless, agreeably aromatic smelling fluid; soluble in all proportions in water and alcohol; boils at  $38^{\circ}$ , and corresponds gassiform to 6 volumes gas. If some potassa be added to the aqueous solution, thus, under production of wood-spirit and formate of potash, a colorless fluid, *methylal* is formed; it boils at  $42^{\circ}$ , sp. gr. 0.8581; requires three parts water for solution, and consists of  $\text{C}_6\text{H}_8\text{O}_4 = (\text{C}_2\text{H}_3)\text{O}, (\text{C}_4\text{H}_5)\text{O}_3 = \text{MeO}, \text{HO} + \text{MeO}, \text{FoO}$ . If methylal be exposed to the action of chlorine, we obtain a fluid combination, which consists of  $\text{C}_6\text{HCl}_3\text{O}_3 = (2\text{C}_2\text{Cl}) \left\{ \begin{array}{l} \text{O}_2 \\ \text{Cl} \end{array} \right. + (\text{C}_2\text{H})\text{O}(?)$

*Chlorformate of Methyl:*  $\text{MeO}, (\text{C}_2\text{Cl})\text{O}_3$ , is obtained by the action of wood-spirit upon oxychloride of chlorformyl, accompanied by production of hydrochloric acid. Oily fluid, boils at  $78^{\circ}$ , and possesses a suffocating odor.

*Acetate of Methyl:*  $\text{MeO}, \text{AcO}_3$ , is abundantly formed by distillation of wood. Is obtained by distillation of sulphate of methyl with acetate of soda. Thin, colorless fluid, of agreeable etheric odor and burning taste; boils at  $54^{\circ}$ ; sp. gr. 0.9774. Dissolves in

two parts water, and by chloride of calcium is again precipitated; miscible with alcohol and ether in all proportions. Upon the products of decomposition which are obtained by the action of chlorine, *vide* acetate of oxychloride of formyl.

*Xylit, Mesit, Mesiten*, and *Xylit-naphtha* may be regarded as combinations of oxide of methyl with  $\text{AcO}$  and  $\text{AcO}_2$ .  $\text{Xylit} = \text{MeO}, \text{AcO} + \text{MeO}, \text{AcO}_2$ ;  $\text{Mesit} = \text{MeO}, \text{AcO}$ ;  $\text{Mesiten} = \text{MeOAcO}_2$ , and *Xylit-naphtha*  $2\text{MeO} + \text{AcO}$ . *Xylit* and *mesit* are found in crude wood-spirit; the former boils at  $61.5^\circ$ , the latter at  $71^\circ$ . *Mesiten* is obtained if *xylit* be distilled with equal quantity of sulphuric acid, as well as by the action of hydrate of potassa upon *xylit* simultaneously with *xylit* oil,  $\text{C}_{12}\text{H}_9\text{O}$ , and *xylit* resin,  $\text{C}_8\text{H}_6\text{O}$ . *Mesiten* has the same constitution as acetone, but it boils at  $63^\circ$  (acetone at  $55^\circ$ ).

*Chloracetate of Methyl*:  $\text{MeO}, (\text{C}_4\text{Cl}_3)\text{O}_3$ , is obtained by the action of wood-spirit upon oxychloride of chloracetyl. Agrees in its properties with chlorformate of methyl. *Butyrate of Methyl*:  $\text{MeO}, \text{BuO}_3$ . Colorless, ethereal liquid; boils at  $98^\circ$ ; sp. gr. 0.904. *Valerianate of Methyl*:  $\text{MeO}, \text{VaO}_3$ . Very mobile, water-clear fluid, of aromatic odor; boils at  $114^\circ$ ; sp. gr. 0.920. *Capronate of Methyl*:  $\text{MeO}, \text{CaO}_3$ , quite equals the former compound. *Caprate of Methyl*:  $\text{MeO}, \text{CpO}_3$ . Colorless, mobile liquid, of strong aromatic odor; scarcely soluble in water, but easily soluble in alcohol and ether. *Margarate of Methyl*:  $\text{MeO}, \text{MgO}_3$ , is solid, crystalline, melts in the warm hand, may be distilled without decomposition.

*Formate of Ethyl*:  $\text{AeO}, \text{FoO}_3$ . Metamerie with acetate of methyl. Water-clear fluid, of agreeable odor and taste; soluble in nine parts water; boils at  $54.^\circ 9$ ; sp. gr. 0.944; decomposes in contact with water into alcohol and formic acid. If chlorine be allowed to act upon formate of methyl, we obtain in the beginning a compound the same as formate of oxychloride of acetyl  $= (\text{C}_4\text{H}_5)\text{O}, (\text{C}_2\text{H})\text{O}_3 + (\text{C}_4\text{H}_3) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 \end{array} \right. (\text{C}_2\text{H})\text{O}_3 = \text{C}_6\text{H}_5\text{ClO}_4$ ; we compare formate of oxychloride of acetyl.

*Chlorformate of Ethyl*:  $\text{AeO}, (\text{C}_2\text{Cl})\text{O}_3$ , is obtained by the action of alcohol upon the oxychloride of chlorformyl. Colorless fluid; boils at  $94^\circ$ ; excites a copious flow of tears.

*Acetate of Ethyl* (Acetic Ether):  $\text{AeO}, \text{AcO}_3$ , is found produced in many wines; is best obtained by distillation of ether-sulphate of potassa with acetate of soda. Colorless fluid, of very agreeable odor, and burning taste; dissolves in  $7\frac{1}{2}$  parts water; mixes with alcohol and ether in all proportions. If chlorine be conducted into acetate of ethyl, we obtain, by the first action, a combination similar to acetate of oxychloride of acetyl  $= \text{C}_8\text{H}_7\text{ClO}_4$  (*v.* the last combination).

*Basic Acetate of Ethyl* (Acetal):  $3\text{AeO} + \text{AcO}_3$ , is produced by the slow oxidation of alcohol by means of platinum-black. Color-

less, thin-flowing liquid, smelling like nitric ether; miscible in all proportions with alcohol and ether; dissolves in 6 parts water; boils at  $95^{\circ}.2$ ; sp. gr. 0.833. In contact with platinum-black changes in the air into acetic acid; gives with hydrate of potassa aldehyd-resin, and is, perhaps, a combination of ethyl-oxide with aldehyd,  $(C_4H_5)O + (C_4H_3)O, HO = C_8H_9O_3$ .

*Chloracetate of Ethyl*:  $AeO, (C_4Cl_3)O_3$ . If chloracetic acid salt be distilled with alcohol and sulphuric acid, an agreeable smelling fluid is obtained. *Oxychlor-chloracetate of ethyl* is obtained by the action of chlorine upon the acetate of ethyl.

*Ether-sulphacetic Acid*:  $HO(AeO, C_4H_2, ^\wedge SO_2)^\wedge SO_3$ . Dry sulphaceto-sulphate of silver, diffused in alcohol, is decomposed by a current of dry chlorine gas; we obtain chloride of silver, and a clear fluid, which, evaporated in a vacuum, leaves behind a syrup-thick mass, of sharp, aromatic, etheric taste; completely soluble in water; gives, saturated with oxide of silver, a fatty salt of mother-of-pearl lustre, deliquescent, and consisting of  $AgO, (AeO, C_4H_2, ^\wedge SO_2)SO_3$ .

*Acrate of Ethyl*:  $AeO, AcrO_3$ . Very thin-flowing liquid, of agreeable, aromatic smell; boils at  $63^{\circ}$ . By the presence of bases and water, is converted into acetic ether.

*Propionate of Ethyl*:  $AeO, PrO_3$ . Water-clear fluid, of agreeable fruit odor.

*Butyrate of Ethyl*:  $AeO, BuO_3$ . A thin fluid; colorless, very mobile, easily inflammable, of a pleasant fruit odor, little soluble in water, easily soluble in alcohol, and ether, of sp. gr. 0.904; boiling point  $114^{\circ}.8$ . Occurs in rum.

*Bichlor-butyrates and Quadrichlor-butyrates of Ethyl* are both insoluble, and are not decomposed by cold solution of potassa.

*Valerianate of Ethyl*:  $AeO, VaO_3$ . A water-clear, colorless fluid of peculiar cough-exciting smell, like fruit and valerian; insoluble in water; sp. gr. 0.865; boiling point  $133^{\circ}$ .

*Capronate of Ethyl*:  $AeO, CaO_3$ . Colorless fluid, of pleasant, peculiar smell, and burning taste; sp. gr. 0.882; boiling point  $162^{\circ}$ .

*Oenanthatate of Ethyl*:  $AeO, OeO_3$ . Colorless, agreeable smelling fluid, of burning taste; crystallizes in the cold.

*Oenanthe-Ether*:  $AeO, (C_{14}H_{13})O_2$ , occurs in wine fuselole; in a pure state colorless, of strongly stupefying wine-smell, and sharp, unpleasant taste; in water slightly, but in alcohol and ether, easily soluble.

*Caprate of Ethyl*:  $AeO, CpO_3$ . Colorless, thin-flowing, of pleasant odor, resembling pine-apple; sp. gr. 0.84; boiling point  $214^{\circ}$ .

*Lauro-stearate of Ethyl*:  $AeO, LaO_3$ . Crystallizes at  $-10^{\circ}$  in small spears; sp. gr. 0.86; boiling point  $264^{\circ}$ .

*Ether-myristic Acid*:  $AeO, HO, 2MyO_3$ . A transparent, colorless fluid, soluble in hot alcohol, and ether.

*Margarate of Ethyl*. Solid; fuses at  $22^{\circ}$ , and stiffens into nee-



dles of mother-of-pearl lustre; from an etheric solution at  $8^{\circ}$ , it forms large beautiful crystals of an almost diamond lustre.

*Ether-stearic Acid*:  $\text{AeO}, \text{HO}, \text{Mg}_2\text{O}_5$ . Crystallizes from an alcoholic solution in silky-lustred needles.

*Stearophanate of Ethyl*:  $\text{AeO}, \text{SphO}_3$ . A brownish white, semi-transparent solid, fuses at  $32^{\circ}$ , brittle, nearly odorless, and of butter-like taste.

*Behenate of Ethyl*:  $\text{AcO}, \text{ByO}_3$ . Semi-transparent, inodorous, crystalline, fuses at  $49^{\circ}$ .

*Cerotate of Ethyl*:  $\text{AcO}, \text{CoO}_2$ . A wax-like mass, fuses at  $60^{\circ}$ .  
 Combinations of the oxide of amyl. *Acetate of Amyl*:  $\text{AmO}, \text{AcO}_3$ . Colorless, very thinly-flowing liquid, of ether-like, aromatic odor; lighter than water; boils at  $133^{\circ}$ .

*Valerianate of Amyl*:  $\text{AmO}, \text{VaO}_3$ . A cold saturated solution of acid chromate of potassa is mixed with an excess of sulphuric acid, and then spirits of amyl added. Under evolution of heat, valerianic acid is formed, which remains dissolved in water, and valerianate of amyl, which floats upon the surface. Of a peculiar odor, resembling that of wine-dregs under decomposition.

Combinations of oxide of ethyl. Spermaceti. *Ethalate of Cethyl* (Spermaceti):  $\text{CcO}, \text{AeO}_3 = \text{C}_{32}\text{H}_{32}\text{O}_2$ . Spermaceti occurs in particular cavities of the head of the *Physeter macrocephalus*, *Tursio microps*, *Orthodon*, and *Delphinus edentulus*, in sperm oil dissolved, and is separated after the death of the animal as a white, semi-transparent, brittle, talcose-feeling mass, of a crystalline fracture. By repeated crystallization from boiling alcohol, the yet retained oil is removed; the thus purified sperm is called *Cetin*. Crystallizes from a hot alcoholic solution in slender, white, mother-of-pearl lustred leaves, which fuse at  $49^{\circ}$ , and volatilizes at  $360^{\circ}$ , without decomposition. Gives, by oxidation with nitric acid, pimelinic, adipinic, and succinic acids.

Combination of oxide of cerosinyl: sugar-cane wax. *Cerosinate of Cerosinyl* (Cerosin):  $\text{C}_{43}\text{H}_{43}\text{O} + \text{C}_{43}\text{H}_{47}\text{O}_3 = \text{C}_{48}\text{H}_{43}\text{O}_2$ , occurs upon the surface of sugar-cane. In pure state is white and crystallizable; melts at  $82^{\circ}$ ; insoluble in cold alcohol, but easily soluble in hot; dissolves with difficulty in boiling ether; burns with beautiful white flame.

Compound of oxide of cerotyl. Chinese wax. *Cerotate of Cerotyl* (Chinese Wax):  $\text{C}_{54}\text{H}_{55}\text{O} + \text{C}_{54}\text{H}_{53}\text{O}_3 = \text{C}_{54}\text{H}_{54}\text{O}_2$ . The Chinese wax of commerce recrystallized from alcohol and naphtha, washed with ether, and then boiled in water, fuses at  $82^{\circ}$ , and by distillation separates into cerotic acid, and ceroten  $\text{C}_{54}\text{H}_{54}$ .

Compound of oxide of melissyl. Myricin, beeswax. *Palmitate of Melissyl* (Myricin):  $\text{C}_{60}\text{H}_{61}\text{O} + \text{C}_{32}\text{H}_{31}\text{O}_3 = \text{C}_{46}\text{H}_{43}\text{O}_2$ . That part of beeswax insoluble in boiling alcohol is myricin. It may be considered as palmitate of melissyl; is greenish, and fuses at  $64^{\circ}$ . By treatment with an alcoholic solution of potassa, it sepa-

rates into hydrate of oxide of melissyl and palmitate of potassa. If myricin or common wax be treated a long time with nitric acid, we thus obtain pimelinic, adipinic, lipinic, and succinic acid.

The *white wax* bleached by the sun or by chlorine White wax. is mostly myricin; it is white, tasteless, inodorous; sp. gr. 0.834; below 0° brittle and hard; at common temperatures kneadable; fuses at 66°; requires ten parts boiling ether to dissolve it; is insoluble in cold ether, dissolves partially by boiling alcohol (cerotic acid); furnishes by dry distillation the so-called wax-butter, which is a mixture of palmitic acid, margaric acid(?), paraffin, etc. As is known, the cells Wax-butter. of the bee consist mostly of wax; this originates in part from the vegetable matter upon which the bee feeds; yet the greater part of the wax which the bee exudes from between the abdominal rings, is a product of the vital functions of those organs; for the bees continue to make wax, if they be fed with pure honey. In this case, it can only be formed by the deoxidation of sugar.

By *palm wax*, we understand that wax occurring upon the bark of *Ceroxylon andicola*, a tree growing in New Grenada. It fuses at 70°, and must consist Appendix to  
wax. Palm  
wax. of  $C_{72}H_{72}O_4 = C_{36}H_{36}O_2$ . *Cernauba wax* has also the Cernauba wax. same constitution; it forms a thin covering to the surface of the leaves of the cernauba palm, and is dissolved away after the drying of the leaves. From the boiling alcoholic or etheric solution it is separated crystalline; fuses at 63°, easily pulverizable.

*Myrica wax* is obtained by boiling the berries of Myrica wax. several species of *Myrica*, particularly *Myrica cerifera*, a tree growing abundantly in Louisiana. It is green and brittle, fuses at 37°, sp. gr. 1.05, and in pure state must consist of  $C_{36}H_{36}O_5$ . Of the same constitution must be also the *Ocuba wax*, which is probably procured from the kernel of the *Myrista ocuba*, a shrub occurring in the province Ocuba wax. of Pera; it is yellow, and fuses at 36°.

*Leaf wax* occurs in intimate combination with Leaf wax. chlorophyl in the grasses and leaves. The green leaves are expressed, dried, and treated with boiling alcohol; after cooling, the wax is precipitated with green color; soft, viscid, and soluble in boiling alcohol. The green color is caused by chlorophyl.

*Cork wax* occurs in the bark of the cork-tree Cork wax. (*Quercus suber* L.), and is obtained by extraction with strong alcohol. After evaporation of the alcohol, we obtain the wax in yellow crystals. It consists of  $C_{25}H_{20}O_3$ , and treated with nitric acid must give an acid, ceric acid, consisting of  $HO, C_{14}H_{10}O_8$ . Ceric acid.

## SECOND CLASS.

## HYDROPOLYCARBYLS.

*First Group.*Carbon Nucleus:  $C_2$ .

The first group of the Hydropolycarbyls consists of:—

- a. *The Allyl Group*, and
- b. *The Oleyl Group*.

## ALLYL GROUP.

Component  $C_2H_2$ ; Nucleus  $C_2$ ; Active element H.

To the radicals of this group belong:—

- |                  |  |
|------------------|--|
| Member 2. Allyl, | $All = 2C_2H_2, C_2, H = C_6H_5.$      |
| “ 3. Odmyl,      | $Od = 3C_2H_2, C_2, H = C_8H_7.$       |
| “ 5. Ferulyl,    | $Fe = 5C_2H_2, C_3, H = C_{12}H_{11}.$ |

## SECOND MEMBER.

 $All = 2C_2H_2, C_2, H = C_6H_5.$ 

## ALLYL.

*Occurrence.*—Garlic oil, which is procured by distillation of the bulbs of *Allium sativum*, (garlic) with water, is a mixture of oxide of allyl with sulphur-allyl. The same oil is probably found also in the plant *Alliaria officinalis* (*Erysimum aliararia*, in the plant *Thlaspi arvensis*, in common with the so-called volatile oil of mustard, which may be considered as a compound of sulphur-allyl with sulphur-cyanogen. The same mixture can also be obtained from the seeds of *Thlaspi arvensis* yet it is not already completely formed in the same, but arises by a process of fermentation. From the root of the *Alliaria officinalis* we obtain only oil of mustard.

The *Crude Garlic-oil*, as it is procured by distillation of garlics with water (1 cwt. garlics give 3 to 4 oz. oil), is a yellowish-brown, oily fluid, sinking in water, of peculiar offensive garlic odor. If this fluid be heated to  $150^\circ$ , it begins to boil, and now commences instantaneously a rapid heating, accompanied by continual decomposition, by which a vapor escapes of insupportable suffocating smell; no trace of oil goes over, and a black glutinous mass remains as residue.

If the crude garlic-oil be distilled over a salt-bath, the volatile part of the oil goes over soon, even before the fluid boils, and thus is produced the purified garlic-oil; it is lighter than water, and suffers no change by boiling;

it possesses a pale, yellow color, and a strong, unpleasant garlic smell. This oil behaves toward reagents like sulphur-allyl.

If we let potassium act upon the pure water-free oil, the latter is covered with a leather-brown layer, which consists of sulphide of potassium, potassa and a resinous substance, whilst at the same time a small quantity of gas escapes, which burns with pale, blue flame. If, when the evolution of gas has ceased, the fluid be quickly distilled from the sediments, it will not be farther attacked by potassium, and exhibits pure sulphur-allyl,  $\text{AllS}$ ; probably in the pure garlic oil a compound of  $\text{AllS} + \text{HS}$  occurs.

The purified oil is a mixture of oxide of allyl and sulphur-allyl.

*Allyl Oxide* possesses the property of forming with nitrate of silver a crystalline compound, which consists of  $\text{AlLO}, \text{AgO}, \text{NO}_5$ . This compound is formed directly by the use of oxide of allyl; and also by the employment of sulphur-allyl; it is formed by double decomposition, and the separation of sulphide of silver. If, now, to a concentrated alcoholic solution of nitrate of silver, pure garlic-oil be cautiously added, in this manner, very often, even before the separation of sulphide of silver, the above-mentioned compound will be formed, which can only result from the presence of oxide of allyl.

*Oxide of Allyl*:  $\text{AlLO}$ . If nitrate of silver-allyl (Silver oxyd-allyl oxyd) be treated with ammonia, nitrate of silver-ammonia, and oxide of allyl are formed; the last of which separates. Completely colorless, oily fluid of peculiar disagreeable smell; possesses a strong tendency to absorb oxygen.

Combination of allyl with oxygen.

*Nitrate of Silver-allyl* (Silver oxyd-allyl oxyd):  $\text{AlLO} + \text{AgO}, \text{NO}_5$ . To an alcoholic solution of nitrate of silver add oxide of allyl by drops, and there are formed crystals, which fill the entire fluid. In dry state, a white shining powder, which is quickly blackened when exposed to light and heat, without undergoing a perceptible decomposition. Not easily soluble in cold alcohol and ether; easily dissolved by water; burns by heating with quick, feeble explosion. It is quickly decomposed by *fuming nitric acid*. *Hydrochloric acid* precipitates chloride of silver. Brought in contact with *ammonia*, at once oxide of allyl is separated.

*Sulphur-allyl*:  $\text{AllS}$ . The production from pure garlic-oil is given above. A completely colorless water-clear fluid, powerfully refracting light, possessing a garlic odor, lighter than water, in which it is not easily soluble, but easily soluble in alcohol and ether. It can be distilled without decomposition. (For formation of sulphur-allyl from mustard oil, see this.) *Fuming nitric acid* decomposes the combination, forming sulphuric and oxalic acid. *Concentrated sulphuric acid* dissolves, without decomposing it, with a reddish purple color; it absorbs hydrochloric acid gas in great quantity. The deep

Allyl and sulphur.



indigo-blue fluid, after standing long in the air, is bleached by being heated and thinned with water.

Sulphur-allyl combines with the sulphides of several metals, forming sulpho-salts, in which it takes the place of a base. The *Mercury compound*,  $\text{AlIS} + 2\text{HgS}$ , appears to be formed, if the combination of sulphide of mercury-allyl with chloride of mercury-allyl (*vide* below) be treated, first with potassa and then with dilute nitric acid; completely white body.

*Silver Compound*:  $\text{AlIS} + \text{AgS}(?)$ , is obtained, when a solution of nitrate of silver in ammonia is mixed with an excess of sulphur-allyl; the oxide of allyl is separated, whilst often a white precipitate is produced, which, after remaining a long time, is decomposed by the volatilization of sulphur-allyl.

*Platinum Compound*:  $\text{AlS} + \text{PtS}_2$ . The double compound of platinum-sulpho-salt with "chlor-platin-allyl" is treated a long time with sulphide of ammonium; ale-brown, insoluble in water, alcohol, and ether. Is decomposed at  $100^\circ$ , accompanied by evolution of sulphur-allyl. *Palladium Compound*:  $2\text{AlS} + 3\text{PdS}$ . We add a small quantity of an aqueous solution of pure garlic oil to an excess of the nitrate of protoxide of palladium, also dissolved in water. A loose, light-brown precipitate; when dried exhibits a tasteless powder; insoluble in water, alcohol, and ether; loses at  $100^\circ$ , sulphur-allyl. *Gold Compound*: a solution of chloride of gold gives with sulphur-allyl a beautiful yellow precipitate, which soon clings together like resin, and covers itself with metallic gold.

*Chlor-allyl* is not known by itself. Combinations of the same are:—

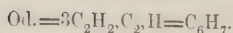
*Sulpho-chlor-mercury-allyl*:  $(\text{AlIS} + 2\text{HgS}) + (\text{AlI Cl} + 2\text{HgCl})$ . If concentrated alcoholic solution of purified garlic oil and of bichloride of mercury be mixed with each other, there is formed a white precipitate, which is increased by dilution with water. If this precipitate be boiled with alcohol, the compound is dissolved, whilst a great part of the precipitate remains undissolved. By dilution with water, the compound separates from the alcoholic solution; a tolerably heavy, perfectly white powder, insoluble in water, not easily soluble in alcohol and ether, blackens in the sunlight. If overflowed with a concentrated solution of potassa, there are separated oxide of mercury, and a body which probably consists of  $\text{AlIS} + 2\text{HgS}$ .

*Sulpho-chlor-platinum-allyl*:  $(2\text{AlIS} + 3\text{PtS}_2) + (\text{AlI Cl} + \text{PtCl})$ . If to an alcoholic solution of rectified garlic oil an alcoholic solution of chloride of platinum be added, and the mixture diluted with water, a yellow precipitate falls resembling the chloride of platinum and ammonium; insoluble in water, and soluble with difficulty in alcohol and ether. Hydro-sulphuric acid does not react upon the compound; decomposes at  $100^\circ$ .

Allyl and chlorine.

## THIRD MEMBER

## ODMYL.

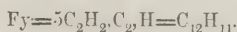


*Formation.*—This radical is known only in combination with sulphur. It is formed when sulphur with fatty oils, which contain oleic acid, are submitted to dry distillation. (Margaric acid and stearic acid do not give this compound.) If we warm sulphur with fatty oils, for instance, linseed oil, it is gradually dissolved, and forms a thick, dark mass, called *balsam sulphuris*. By increased heat, a violent action commences, hydrosulphuric acid being evolved, whilst simultaneously an oil goes over resembling garlic oil. This oil begins to boil at  $71^\circ$ ; but the boiling point continually rises. If to an alcoholic solution of the oil we add an alcoholic solution of bichloride of mercury, there is produced a white precipitate; and if the same be decomposed by hydrosulphuric acid, there goes over by distillation a pure oil lighter than water. This is the

*Sulpho-hydro-odmyl:*  $\text{OdS} + \text{HS}$ . Possesses an unpleasant garlic odor, and gives with perchloride of mercury a precipitate of white, mother-of-pearl lustre, consisting of  $(\text{OdS}_2 + 2\text{HgCl}) + (\text{OdS} + 2\text{HgS})$ . With an alcoholic solution of platinum, a precipitate is obtained, which is constituted of  $\text{C}_{16}\text{H}_{14}\text{S}_5\text{Pt}_2\text{Cl}_2 = (\text{OdS}_2 + \text{PtCl}) + (\text{OdS}_2 + \text{PtS})$ .

## FIFTH MEMBER.

## FERULYL.



*Occurrence.*—Sulphoferulyl occurs in assafetida (*resin of ferula asafetida*), and possesses the offensive smell of that substance.

*Sulpho-ferulyl* (Assafetida Oil):  $\text{FyS}$  and  $\text{FyS}_2$ . Pulverized assafetida is with water in a glass retort distilled over a salt bath. The oil which goes over is light yellow, of a most disagreeable smell, somewhat soluble in water, easily soluble in alcohol and ether. After standing a long time it is decomposed, hydrosulphuric acid being evolved. The oil begins to boil at  $135$  to  $140^\circ$ , whereby it is decomposed, with evolution of hydrosulphuric acid. This crude oil is probably a mixture of simple and double sulphoferulyl. If this oil be distilled in a current of ammonia gas, there is deposited, at  $150^\circ$ , in the neck of the retort, white, shining, extremely volatile crystal scales, of sulphide of ammonium. If we heat the oil with simple and quintuple sulphide of potassium, it evolves at  $185^\circ$  hydrosulphuric acid, whilst the color of the oil grows always darker. *Hydrochloric Acid Gas* gradually colors the oil black; *chlorine* produces the same change of color, under the evolution of hydrochloric acid, and the formation of chloride of sulphur.

*Concentrated Nitric Acid* reacts violently, even to the inflammation of the oil, under the production of acetic, propionic, and oxalic acid, and a resinous substance. In the same manner acts *Chromic Acid*. If we digest the crude oil a long time with *hydrate of lead*, or if we lead into the same *Sulphurous Acid Gas*, we obtain a rosemary smelling oil, which consists of  $C_{48}H_{45}S_9 = 4(C_{12}H_{11})S_2 + HS$ . The same compound is also obtained together with valerianic and propionic acids, if the crude oil be conducted over heated potassa lime. If we heat the crude oil with *hydrate of soda* to  $120^\circ$ , hydrosulphuric acid is abundantly evolved, and as residue formate and acetate of soda remain, together with an oil consisting of  $C_{36}H_{33}S_2$ .

The alcoholic solution of the crude oil gives with *chloride of platinum*, according to the concentration, temperature, and time of acting, variously constituted yellow and brown precipitates, which consist of sulpho ferulyl-sulpho platinum, with one, two, or three atoms of chlorferulyl-chlorplatinum  $= (FyS_2 + PtS_2) + 1, 2,$  and  $3 (FyCl + PtCl_2)$ . Besides, the precipitates have an admixture of sulphide of platinum. With perchloride of mercury, the alcoholic solution of the crude oil gives a white, flaky precipitate; the residual fluid gives an acid reaction, and a garlic odor. If the precipitate be boiled with alcohol, there remains a grayish white powder, which is said to consist of  $(C_{12}H_{10}S_8 + 2HgS) + 4Hg_2Cl + Hg_3S_2Cl$ . From the alcoholic solution, whilst cooling, is precipitated a white salt in microscopic crystals  $= (C_{12}H_{10}S_2 + 5HgS) + (C_{12}H_{10}Cl_2 + HgCl)$ .

### The Oleyl Group.

Component  $C_2H_2$ ; Nucleus  $C_2$ ; Active part  $C_2H$ .

With the oleyl group the following radicals may be classed:—

Member 1. Terecyl,	Tr = $C_2H_2, C_2, C_2H = C_6H_3$ .
“ 3. Angelicyl,	Ag = $3C_2H_2, C_2, C_2H = C_{10}H_7$ .
“ 13. Moringyl,	Mo = $13C_2H_2, C_2, C_2H = C_{30}H_{27}$ .
“ 16. Oleyl,	Ol = $16C_2H_2, C_2, C_2H = C_{36}H_{33}$ .
“ 17. Doeglyl,	Do = $17C_2H_2, C_2, C_2H = C_{38}H_{35}$ .
“ 20. Erucyl,	Er = $20C_2H_2, C_2, C_2H = C_{44}H_{41}$ .

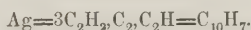
Whether the radicals of the oleyl group behave to those of the allyl group as those of the formyl to those of the methyl group, the insufficiency of previous investigations does not allow us to determine. Like those of the formyl group they all combine with three atoms of oxygen to form acids. But whilst the lower members of the acids of the formyl series are fluid at common temperatures, and the higher are solid, in the acids of the oleyl group an inverse condition exists. The higher members are called oleic acids, because they are the most essential acids of the fats which are fluid at common temperature; they occur in combination with

oxide of glycyI always in company with the solid, fatty acids, as margaric acid and stearic acid.

*Terecric Acid*:  $\text{HO}, \text{TrO}_4(?)$ . This acid, yet little known, is formed simultaneously with terebinic acid, terephthalic and terebenzinic acid, by the action of nitric acid upon oil of turpentine; we obtain, after decomposition has ceased, a resinous substance, insoluble in water and alcohol, which consists of a resinous body, terephthalic and terebenzinic acid, and an acid fluid, in which are found together, free nitric, oxalic, terebinic, and terecric acid. If the acid solution be concentrated, and then left a little while standing, the oxalic acid and the terebinic acid are deposited, and the terecric acid is dissolved in the mother liquor. We evaporate the liquor until it forms a doughy mass, dilute the same with water and saturate with carbonate of baryta, filter from the precipitate and decompose the terecrate of baryta found in the solution by sulphuric acid. After evaporating the aqueous solution, we obtain the acid as an orange-yellow, uncrystallizable mass, of a sour and afterward astringent and bitter taste, which is decomposed by heating, and forms with oxide of lead a salt of microscopic crystals, which consists of  $\text{PbO}, \text{C}_6\text{H}_3\text{O}_4$ .

## THIRD MEMBER.

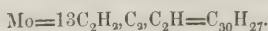
## ANGELICYL.



*Angelic Acid*:  $\text{HOAgO}_3$ , is found with valerianic acid in the root of the *Angelica officinalis*. The dry roots are boiled in 3 to 4 parts hydrate of lime and water, the filtered solution is concentrated, then over-saturated with sulphuric acid and distilled. From the distillate, after a little time, the angelic acid crystallizes. It appears in rather transparent, colorless crystals, which give a sour reaction; fuse at  $45^\circ$ , and after cooling stiffen to a shining mass; possessing an aromatic odor; not easily soluble in cold water, but easily soluble in alcohol and ether; boils at  $190^\circ$ ; undecomposed distillable. If the salts be evaporated in the air, they lose a great part of their acid; the compounds with alkalies are easily soluble in water and alcohol. The *earthy salts* dissolve in water. The *lime salt* crystallizes in shining leaflets. The *lead salt* appears in beautiful perfect crystals, not easily soluble in water. The *salts of peroxide of iron* give with the alkaline salts of angelic acid, a flesh-red precipitate.

## THIRTEENTH MEMBER.

## MORINGYL.

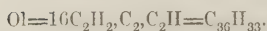


*Moringaic Acid*:  $\text{HO}, \text{MoO}_3$ , is found with behinic acid in the oil of *Moringa aptera*. Fluid; stiffens crystalline at  $0^\circ$ ; specific gravity 0.908.



## SIXTEENTH MEMBER.

## OLEYL AND OLYL.



*Hydrate of Oleinic Acid* (Oleic Acid):  $\text{HO}, \text{OIO}_3$ . Oleic acid occurs in most fats, particularly in the fluid, in combination with oxide of glyceryl. A few of these oils possess the property, when they are exposed in thin layers to the air, of being converted into a greasy mass under absorption of oxygen, whilst others form dry, varnish-like bodies; the former are called not drying, and the latter drying oils. The cause of this variety of behavior lies in the difference of the liquid fatty acids occurring in the oils; but which are probably constituted alike. The not drying acid is called *oleinic* and also *oleic* acid, and the drying, *olinic* acid. The production of the pure acids is difficult on account of the great tendency of the, same to a higher oxidation. In order to obtain oleic acid, oil of bitter almonds is saponified with potassa, and the obtained soap decomposed by hydrochloric acid. The separated mixture of oleic and margaric acid is digested a few hours with oxide of lead at  $100^\circ$ , and the mixture left a little while in contact with ether, which dissolves the oleate of lead. The solution of ether is mixed with the same volume of water, then as much hydrochloric acid added as is necessary for complete decomposition, and the mixture powerfully shaken. The oleic acid remains dissolved in the ether. After the evaporation of the etheric solution, there remains behind a mixture of pure oleic acid with oxidized acid; if this mixture be exposed to a temperature of  $-7^\circ$ , the pure acid crystallizes, whilst the oxidized acid remains dissolved. Pure oleic acid appears at lower temperature in white shining needles, which melt at  $14^\circ$  to an inodorous, tasteless, and colorless liquid, which does not redden litmus, and at  $4^\circ$ , under strong contraction, grows stiff; is insoluble in water, but easily soluble in alcohol. In the solid form it is unchangeable in the air, but in a melted state it oxidizes, and forms *oxidized oleic acid*, which should consist of  $\text{HO}, \text{C}_{36}\text{H}_{33}\text{O}_4$ . If we let oleic acid oxidize at  $100^\circ$ , thus will be obtained carbonic acid, and a new acid, which will be constituted of  $\text{HO}, \text{C}_{34}\text{H}_{32}\text{O}_4$ . If we bring pure oleic acid in contact with *nitrous acid* it is converted into an acid, which melts at  $44^\circ$ ; gives a powerfully reacting acid—the *elaidic acid*, which has the same constitution as the oleic acid. Elaidic acid crystallizes from an alcoholic solution in broad leaves; in a melted state it oxidizes to form an acid, no longer becoming solid, which must consist of  $\text{HIO}, \text{C}_{36}\text{H}_{33}\text{O}_6$ . *Sulphurous acid* produces the same change.

If oleic acid be boiled a long time in a retort with dilute nitric acid, in the acid distillate are found butyric, valerianic, capronic, oenanthic, capric, pelargonic, and caprinic acid; and in the re-

sidue lipinic, adipinic, pimelinic acid, etc. By *dry distillation* oleic acid gives sebacic, capric, and caprinic acid. By the formation of sebacic acid, oleic acid differs from all other acids. Heated with *sulphur*, it gives sulphide of odmyl (which see).

The pure *Oleic Acid Salts* are scarcely known; what, until recently, were considered as such, were a mixture of oleic acid with oxidized oleic acid compounds.

The *Alkaline Salts* contain much water, and are soluble in the same, as also in alcohol; brought in contact with much water, they separate, in the same way as the margaric and stearic acid compounds, into free alkalies and acid salts. The oleates of alkalies quickly oxidize in the air. Combinations with the *earths, alkaline earths, and oxides of the heavy metals*, are insoluble in water.

The *Lead Salt* is remarkable for its solubility in ether. It has already been shown, in connection with margaric acid, that, by mixing sweet oil with sulphuric acid, margaric-sulphuric acid, together with *olein-sulphuric acid*, is formed, and that the latter, brought in contact with water, separates into *Meta-oleic* and *Hydro-oleic Acid*. Without doubt, these acids oxidize also in the air, and the hitherto received formulæ are probably wrong. If hydro-oleic acid be submitted to dry distillation, we obtain oleen and elaen.

Meta-oleic acid,  
and hydro-oleic  
acid.

*Olinic Acid* (Dry Oleic Acid). It is found in the drying oils, as in linseed oil, hempseed oil, poppy oil, and nut-oil. It is obtained like the not drying oleic acid, with which it agrees in most properties; but it gives, with nitrous acid, no compounds corresponding to elaidinic acid. By boiling with nitric acid, we obtain suberic acid in large quantity.

Olinic acid.

*Hydrate of Doeglinic Acid*:  $\text{HO}, \text{DoeO}_3$ . This acid occurs in train-oil (doeglinthran) and is extracted therefrom in the same manner as oleic acid from almond oil. It is solid at a few degrees above  $0^\circ$ ; in the melted state, yellow; reddens litmus. If train-oil be rapidly distilled, there goes over, with other products, a fluid consisting of  $\text{C}_{12}\text{H}_{12}$  (oleen?).

17th Member.

Doeglyl: Doe.

$17\text{C}_2\text{H}_2, \text{C}_2, \text{C}_2\text{H}$

$=\text{C}_{39}\text{H}_{35}$

*Hydrate of Ricinic Acid*:  $\text{HO}, \text{C}_{38}\text{H}_{35}\text{O}_5$ . The oil of the seed of *Ricinus communis* consists of palmitate and ricinate of glycy. We obtain the acid from *Ricinus oil*, like the oleic acid from almond oil. At common temperature, it forms an inodorous, clear, wine-red acid of syrup thickness, and unpleasant, sharp, burning taste; specific gravity 0.940; it stiffens at from  $-6$  to  $-10^\circ$ ; mixes with alcohol and ether in all proportions; the alcoholic solution gives an acid reaction. By dry distillation we obtain oenanth oil and oenanthic acid. By the action of *nitrous acid* upon ricinus oil, we obtain a white wax-like mass—*Palmin*. If the same be saponified with potash-lye, and the soap decomposed by an acid, we thus procure

Ricinic acid.

Palmitic acid.

*palmitic acid*, which crystallizes in silky, stelliform needles, melts at  $50^{\circ}$ , and, probably, arises out of ricinic acid in the same way as elaidic acid out of oleic acid.

*Ricinic Acid Salts.* Ricinic acid expels carbonic acid from its combinations. Nearly all the salts, even those with the alkaline earths, and metallic oxides, possess the property of crystallizing; neither the acids, nor their salts, are oxidized in the air. According to another investigation, ricinic acid consists of  $\text{HO}, \text{C}_{36}\text{H}_{33}\text{O}_5$ .

20th Member.

Erucyl:

$\text{Er. } 20\text{C}_2\text{H}_5, \text{C}_2$

$\text{C}_2\text{H}=\text{C}_{44}\text{H}_{41}$

*Hydrate of Erucic Acid:*  $\text{HO}, \text{ErO}_3$ . This acid occurs in the fatty oils of the black and the white mustard seeds. According to its constitution, it belongs in the series of the oleyl group, but in its properties it is allied to the solid fatty acids. The oil is saponified, and the acid-mixture, separated from the soap by hydrochloric acid, is digested with oxide of lead; the dry mass is digested with ether, and the undissolved part treated with hydrochloric acid and alcohol. Out of the fluid, filtered from the chloride of lead, erucic acid is procured by evaporation. It crystallizes in shining needles, which melt at  $34^{\circ}$ ; in the solution of ether a lead salt occurs, whose acid is oily, and consists of  $\text{HO}, \text{C}_{38}\text{H}_{35}\text{O}_3$ ; it has, therefore, the same constitution as doeglinic acid.

Salt-like combinations of the oxides of the methyl group and the acids of the oleyl group.

*Oleate of Ethyl.* It is not known in a pure state. Colorless; oily fluid; sp. gr. 0.871.

*Elaidate of Ethyl.* Oily; colorless fluid; inodorous in the cold; of 0.865 specific gravity.

*Doeglinatate of Ethyl.* Yellow, oily fluid. Other compounds are not known.

#### PAIRED DOUBLE RADICAL, CONSISTING OF THE RADICALS OF THE OLEYL GROUP WITH FORMYL.—THE SUCCYL GROUP.

By the action of nitric acid upon margaric, stearic, and oleic acid, are formed, besides formic, acetic, propionic, butyric acid, etc., another series, which occur in the acid fluid, namely succinic, lipinic, adipinic, and pimelinic acid; here also belongs sebamic acid, which arises by dry distillation of oleic acid. These acids agree with each other in their chemical properties, like the acids of the formyl series; they are solid, crystallizable, volatile, and, in the presence of bases, precipitate the salts of peroxide of iron; are very permanent, soluble in water and alcohol, and form an ascending group. As has already been remarked in the General Part, these acids must be viewed as bi-basic, and contain 6 atoms oxygen. These acids may be considered as double acids, consisting of the acids of the oleyl group, and formic acid, resembling the paired double acids of the acetyl compounds with those of formyl. According to this view, the above-named acids correspond to the following formulæ:—

Hydrate of Succinic Acid	$2\text{HO}, (\text{C}_6\text{H}_3)\text{O}_3, \text{---} (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{C}_8\text{H}_4\text{O}_6.$
“ Lipinic “	$2\text{HO}, (\text{C}_8\text{H}_5)\text{O}_3, \text{---} (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{C}_{10}\text{H}_6\text{O}_6.$
“ Adipinic “	$2\text{HO}, (\text{C}_{10}\text{H}_7)\text{O}_3, \text{---} (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{C}_{12}\text{H}_8\text{O}_6.$
“ Pimelinic “	$2\text{HO}, (\text{C}_{12}\text{H}_9)\text{O}_3, \text{---} (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{C}_{14}\text{H}_{10}\text{O}_6.$
“ Suberic “	$2\text{HO}, (\text{C}_{14}\text{H}_{11})\text{O}_3, \text{---} (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{C}_{16}\text{H}_{12}\text{O}_6.$
“ Sebacic “	$2\text{HO}, (\text{C}_{18}\text{H}_{15})\text{O}_3, \text{---} (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{C}_{20}\text{H}_{16}\text{O}_6.$

However, these acids may also be considered as combinations of  $(\text{C}_6\text{H}_3)\text{O}_3$  with the ascending members of the acids of the formyl group. Then the formulæ are:—

Hydrate of Succinic Acid	$2\text{HO}, (\text{C}_6\text{H}_3)\text{O}_3, \text{---} (\text{C}_2\text{H})\text{O}_3.$
“ Lipinic “	$2\text{HO}, (\text{C}_6\text{H}_3)\text{O}_3, \text{---} (\text{C}_4\text{H}_3)\text{O}_3.$
“ Adipinic “	$2\text{HO}, (\text{C}_6\text{H}_3)\text{O}_3, \text{---} (\text{C}_6\text{H}_5)\text{O}_3, \text{etc.}$

*Succinic Acid*:  $\text{SuO}_6.$

*Occurrence and Formation.*—*Succinic acid* occurs in amber; it is formed by the action of nitric acid upon margaric and oleic acid, Japanese wax, beeswax, etc.; it farther arises from the fermentation of asparagin, and of malate of lime, under the influence of decayed cheese.

*Anhydrous Succinic Acid*:  $\text{SuO}_6$ , is obtained by heating the hydrate with anhydrous phosphoric acid; it melts at  $145^\circ$ , and boils at  $250^\circ$ ; in contact with water is converted into the hydrate. If we expose the hydrate of succinic acid a long time to the temperature of  $140^\circ$ , it loses half of the water under sublimation; completely white, slender needles, of a silky lustre, not easily soluble in water and alcohol, fusing at  $160^\circ$ , but already sublimates at  $140^\circ$ , boils at  $242^\circ$ . The formula of the acid is  $\text{HO}, \text{SuO}_6$ .

Anhydrous succinic acid.

Proto-hydrate of succinic acid.

*Hydrate of Succinic Acid*:  $2\text{HO}, \text{SuO}_6$ . *Production from amber.* Amber is heated in a retort until the swelling up ceases, and a thick oil goes over; the succinic acid sublimes and is purified by pressing, dissolving, and by boiling with a little nitric acid. The so-called *colophonium succini*, which is used in varnish, remains as residue. From the alcoholic solution we obtain the acid in crystals.—*From margaric and stearic acid.* These bodies are treated with nitric acid in the heat, until a clear solution of nitric acid is formed; this we evaporate as far as possible, pour water of  $20$  to  $30^\circ$  over the residuc, remove the oil which is separated, and evaporate the fluid (freed from fat) by gentle heat to crystallization.—After cooling, a granulous mass is separated, which is dried, and by gentle sublimation the succinic acid is obtained.—By *fermentation of malate of lime*. A mixture of 12 parts malate of lime with 40 parts water, and one part of putrid cheese mixed with water, is suffered to ferment at  $30$  to  $40^\circ$ . When the evolution of gas has ceased, the



granulous deposit is washed with water, and then dilute sulphuric acid is added so long as effervescence continues; now we add more sulphuric acid, and boil until the precipitate no longer appears granulous; filter and evaporate the solution to crystallization; the crystals of succinic acid, impure by admixture of gypsum, are purified by sublimation, or by repeated crystallization from alcohol. From the aqueous solution succinic acid crystallizes in large, regular, clear prisms; they melt at  $180^{\circ}$ , and boil at  $235^{\circ}$ ; leave by sublimation no residue. The vapor possesses a sharp smell, and excites violent coughing. The acid is odorless, of a sour, warming taste, dissolves in 25 parts cold water, in 3 parts boiling water, and in  $2\frac{1}{2}$  parts boiling alcohol.

If succinic acid be heated with an excess of hydrate of potassa, we obtain oxalic acid under evolution of combustible gas; distilled with *chromic* and *sulphuric acid*, acetic acid is formed. If we conduct the vapor of *anhydrous sulphuric acid* upon succinic acid, we obtain succin-sulphuric acid.

*Succinic Acid Salts.*—Succinic acid belongs to the stronger organic acids, and forms with bases salts, both soluble and insoluble in water. The soluble give a yellowish-red precipitate with the neutral and basic salts of peroxide of iron. If the insoluble salts be heated in a tube with acid sulphate of potassa, the succinic acid sublimes. The alkali salts correspond to the formula  $2\text{BO}, \text{SuO}_6$ ;  $\text{BO}, \text{HO}, 2\text{SuO}_6$ , and  $\text{BO}, 2\text{HO}, 2\text{SuO}_6$ . Most compounds with the heavier metallic oxides contain one atom acid to two atoms base; nevertheless, a few basic compounds are also known, as with oxide of lead and peroxide of iron. None of these salts suffer decomposition at  $200^{\circ}$ .

*Succinate of Ammonia:*  $2\text{NH}_4\text{O} + \text{SuO}_6$ . A solution of ammonia saturated with succinic acid is evaporated over caustic lime in a vacuum. Transparent, six-sided prisms, easily soluble in water and alcohol; loses ammonia in the air, and is converted into the *acid salt*,  $\text{NH}_4\text{O}, \text{HO}, \text{SuO}_6$ , which crystallizes in transparent, six-sided prisms, of acid reaction. By sublimation, both combinations Bisuccinamid. are converted into *bisuccinamid*  $= \text{NH}, \text{SuO}_4 = \text{NH}$ ,

$(\text{C}_6\text{H}_3)\text{O}_2, (\text{C}_2\text{H})\text{O}_2$ . This last crystallizes from a boiling aqueous solution in six-sided needles, which are almost insoluble in alcohol, dissolve in 9 parts boiling water, and in 220 parts cold water.—*Succinate of Potassa*,  $2\text{KO} + \text{SuO}_6 + \text{aq}$ . Crystallizes in thin rhombic plates; the acid salt,  $\text{KO}, \text{HO}, \text{SuO}_6$ , appears in six-sided needles. If we dissolve this salt in water, and add one atom hydrate of succinic acid, we obtain crystals of  $\text{KO}, 2\text{HO}, 2\text{SuO}_6 + 3\text{aq}$ .—*Succinate of lime*,  $2\text{CaO} + \text{SuO}_6 + 3\text{aq}$ , is obtained when the corresponding potassa salt is precipitated with chloride of calcium; it is deposited in acicular crystals. The acid salt,  $\text{CaO}, \text{HO}, \text{SuO}_6$ , is obtained by saturating a solution of succinic acid with carbonate of lime; often forms soluble crystals a

line in length.—*Succinate of Peroxide of Iron.* If to a solution of  $\text{Fe}_2\text{Cl}_3$ , neutral succinate of potash be added, a voluminous red precipitate is obtained  $= \text{Fe}_2\text{O}_3, \text{SuO}_6$ . If ammonia be poured over this compound while the latter is fresh, a gelatinous mass is formed, which consists of  $18\text{Fe}_2\text{O}_3 + \text{SuO}_6$ .

*Succinate of Lead:*  $2\text{PbO} + \text{SuO}_6$ , is obtained, if to a solution of sugar of lead succinic acid be added. A white, crystalline powder, little soluble in water. If into a warm solution of vinegar of lead, a warm solution of  $\text{NaO}, \text{HO}, \text{SuO}_6$  be brought, a plaster-like precipitate is formed, which after drying consists of  $3\text{PbO} + \text{SuO}_6$ . If we digest the neutral salt,  $2\text{PbO} + \text{SuO}_6$ , with ammonia, a white powder is formed, consisting of  $6\text{PbO} + \text{SuO}_6$ .

*Chlor-succinate of Oxychloride of Chlor-acetyl:*  $2(\text{C}_4\text{Cl}_3) \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 \end{array} \right. + (\text{C}_6\text{Cl}_3, \text{C}_2\text{H})\text{O}_6 = \text{C}_{16}\text{HCl}_{13}\text{O}_8$ . This Derived radical  
of succyl.

combination is formed by the action of chlorine upon succinate of ethyl,  $2\text{AeO} + \text{SuO}_6$ . Snow-white, crystal needles, of penetrating, suffocating smell. If this compound be heated to  $290^\circ$ , carbonic acid is evolved, whilst a thick, oily, smoking fluid goes over, which, when overflowed with water, separates into hydrochloric acid, chlor-acetic acid  $(\text{C}_4\text{Cl}_3)\text{O}_3$ , and into chlor-succinic acid,  $\text{C}_6\text{H}_2\text{Cl}_3\text{O}_3 = \text{C}_2\text{H}_2, (\text{C}_4\text{Cl}_3)\text{O}_3$  (*vide* page 71),  $(\text{C}_6\text{Cl}_3, \text{C}_2\text{H})\text{O}_6 + \text{HO} = \text{C}_6\text{Cl}_3\text{H}_2\text{O}_3 + 2\text{CO}_2$ . If the oily fluid be treated with a concentrated solution of potassa, we obtain chloride of calcium, carbonate, formate, and chlor-succinate of potassa. Warmed with *alcohol* we obtain, upon addition of water, hydrochloric acid, carbonate, chlor-acetate and chlor-succinate of ethyl. Shaken with *ammonia*, we obtain chloride of ammonium, chlor-acetamid and chlor-succinate of ammonia.

*Succin-sulphuric Acid:*  $3\text{HO}, \text{C}_8\text{H}_5\text{O}_3, \sim 2\text{SO}_3 = 3\text{HO}(\text{C}_6\text{H}_2)\text{O}_2 + (\text{C}_2\text{H})\text{O}_3, \sim 2\text{SO}_3$ . The vapor of an- Paired com-  
pound of suc-  
cinic acid.  
hydrous sulphuric acid under cooling, is led slowly over succinic acid. We obtain a brown, glutinous mass; this is dissolved, after 24 hours, in water, and to the solution carbonate of baryta is added, until testing with chloride of barium gives no longer a precipitate; then filter, and completely precipitate the filtrate with a solution of the acetate of lead. The lead salt thus procured, is decomposed by hydrosulphuric acid, and the solution evaporated in a vacuum. A mass of syrup-thickness, in which, after a little time, papillary crystals form; easily soluble in water and alcohol; tastes sour, and gives with bases salts, which contain to 1 atom acid 3 atoms base, 2 atoms base in 1 atom HO, and 1 atom base and 2 HO.

*Hydrate of Lipinic Acid:*  $2\text{HO}(\text{C}_8\text{H}_5)\text{O}_3, \sim (\text{C}_2\text{H})$  Lipinic acid.  
 $\text{O}_3 = 2\text{HO}, \text{LiO}_6$ , is formed from the decomposition of oleic acid, by nitric acid simultaneously with adipinic, pimelinic, and suberic acid, which can all, by crystallization, be separated from the aqueous solution. First appears suberic acid, then pimelinic, later adipinic,

and finally lipinic acid. Lipinic acid appears in long, sharp-pointed crystal leaflets; melts at  $140^{\circ}$ , and forms by heating a powerfully suffocating smoke; sublimes, with the loss of 1 atom  $\text{HO}$ , in long needles. In water somewhat easily soluble, in alcohol and ether soluble in greater quantity. The salt of ammonia crystallizes in long needles. The salts of baryta, strontia, and lime appear as crystalline precipitates.

Adipinic acid. *Hydrate of Adipinic Acid:*  $2\text{HO}, (\text{C}_{10}\text{H}_7)\text{O}_3 \wedge (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{AdO}_6$ . Crystallizes from the aqueous solution in groups; fuses at  $134^{\circ}$ ; sublimes in beautiful feathery crystals. Soluble in all proportions in water, alcohol, and ether.

Pimelinic acid. *Hydrate of Pimelinic Acid:*  $2\text{HO}, (\text{C}_{12}\text{H}_9)\text{O}_3 \wedge (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{PiO}_6$ . Crystallizes in small granules; melts at  $114^{\circ}$ , and stiffens to an opaque radiated mass; sublimes in beautiful, penniform crystals of silky lustre. Is soluble in 35 parts water.

Suberic acid. *Hydrate of Suberic Acid:*  $2\text{HO}, (\text{C}_{14}\text{H}_{11})\text{O}_3 \wedge (\text{C}_2\text{H})\text{O}_3 = \text{SuO}_6$ , is formed by the action of nitric acid upon fat, paper, and linen—upon cork, and the bark of other trees. 1 part of finely-cut cork (or rags, paper), is digested with 6 parts nitric acid of 1.36 sp. gr., until no more nitric-oxygen gas is evolved. When the decomposition is ended, the acid solution is evaporated in a porcelain bowl with constant stirring to remove the free nitric acid; the residue is mixed with a large quantity of boiling water; whilst cooling a wax-like body, and a woody substance, separate, which are removed by filtration. The filtrate is evaporated, until the acid is by cooling separated, in the form of a powder, which is purified by repeated sublimation. The acid, which is separated from the aqueous solution, appears as a white, earthy powder, which melts at  $124^{\circ}$ , and, after cooling, it stiffens to a mass, consisting of fine needles. When cautiously heated, it sublimes, dissolves in 2 parts boiling water, and in 100 parts cold water; 87 parts boiling alcohol take up 100 parts acid; is soluble in  $4\frac{1}{2}$  parts cold alcohol. The suberic acid salts have an acid, briny taste; they are destroyed by red heat, whereby 1 part acid is sublimed unchanged.

Sebacic acid. *Hydrate of Sebacic Acid:*  $2\text{HO}, (\text{C}_{18}\text{H}_{15})\text{O}_3 \wedge (\text{C}_2\text{H})\text{O}_3 = 2\text{HO}, \text{SeO}_6$  is formed by dry distillation of oleic acid. The distillate is boiled out many times with water; from the heated aqueous solution the acid is separated, whilst cooling, in white, acicular, extremely loose crystals of a mother-of-pearl lustre. Tastes feebly acid; melts at  $127^{\circ}$ ; stiffens crystalline; sublimable; easily soluble in boiling water, with difficulty in cold. With the alkalies it gives salts easily soluble in water; with the alkaline earths and heavy metal-oxides, it gives mostly combinations insoluble or soluble with difficulty. From the concentrated alkaline solution the greater part of the acid is pre-



cipitated by stronger acids. By continued boiling with nitric acid, the sebacic acid goes over into pyrotartaric acid.

## APPENDIX TO THE SUCCYL GROUP.

*Camphoric Acid*:  $C_{20}H_{14}O_6 = (6C_2H_2, C_4, C_2H)O_3, \overset{\frown}{(C_2H)O_3} = C_{20}H_{14}O_6$ . Camphoric acid agrees in its chemical relations with succinic acid, and may be considered as a double acid, consisting of formic acid with  $(6C_2H_2, C_4, C_2H)O_3$ , it corresponds therefore to sebacic acid, with the nucleus  $C_4$ .

Sebacic acid  $(7C_2H_2, C_2, C_2H)O_3, (C_2H)O_3 = C_{20}H_{16}O_6$ .  
Camphoric acid  $(6C_2H_2, C_4, C_2H)O_3, (C_2H)O_3 = C_{20}H_{14}O_6$ .

It belongs, therefore, to the succeeding group. It is formed by the action of nitric acid upon camphor.

*Anhydrous Camphoric Acid* is formed by sublimation of the hydrate, and by distillation of ether-camphoric acid. It appears in crystals which belong to the direct prismatic system, with rhombic bases; gives no acid reaction; is at first tasteless, afterwards strongly irritating. In cold water it is scarcely soluble; is again separated anhydrous from the boiling solution; but if it be boiled a few hours with water, it goes over into the hydrate. Alcohol, especially when boiling, dissolves more of it than water. It is most easily soluble in ether; sublimes at  $130^\circ$ , fuses at  $217^\circ$ , and boils at  $270^\circ$ , sp. gr. at  $20.^\circ 5 = 1.194$ . Becomes by rubbing strongly electrical.

*Anhydrous Camphorate of Ammonia*:  $2NH_3 + C_{20}H_{14}O_6 + 2aq$ . If in a hot, anhydrous alcoholic solution of anhydrous camphoric acid, ammonia gas be led to saturation, after cooling, crystals are produced corresponding to the above formula. If the solution of these crystals be evaporated, there is a syrup-like residue, which after a few days stiffens crystalline.

*Camphorammic Acid*:  $NH_3, C_{20}H_{14}O_6$ . We mix a thin aqueous solution of the above salt with hydrochloric acid, and evaporate the solution, crystals of  $NH_3, C_{20}H_{14}O_6$ , are formed. If to the concentrated solution hydrochloric acid be added, amorphous camphoric acid is precipitated.

*Amid-Camphoric Acid*:  $NH_2, C_{20}H_{13}O_6$ , is known only in combination with oxide of lead and oxide of silver. We obtain the lead combination  $PbO + NH_2, C_{20}H_{13}O_6 = PbO, NH_2, (C_{18}H_{13})O_2, \overset{\frown}{(C_2H)O_3} (?)$ , if to a boiling aqueous solution of camphorammic acid acetate of lead be added; it appears in small crystals, which are deposited after cooling.

*Bicamphorimid*:  $NH, C_{20}H_{14}O_6$ . We heat anhydrous camphorate of ammonia, or camphorammic acid, to  $150^\circ$ ; water and ammonia escape, and as residue



imid remains, which crystallizes from boiling alcohol: it may be sublimed in a higher temperature.

*Hydrate of Camphoric Acid:*  $2\text{HO} + \text{CphO}_6$ . One part camphor is subjected to distillation with 7 parts nitric acid; the operation is continued (whilst the acid which has gone over into the retort is poured back) until the camphor is completely dissolved. After the cooling of the acid solution, the camphoric acid crystallizes in small laminated leaves, at first feebly acid, afterwards bitter; melts at  $63^\circ$ , and separates by stronger heat into water and anhydrous acid; 100 parts water at  $12.5^\circ$  dissolve 1.13 parts acid, and at  $96^\circ$  12 parts acid. In alcohol and ether easily soluble. With ammonia camphoric acid gives two combinations, corresponding to the formula  $\text{AmO}, \text{HO}, \text{CphO}_6$ , and  $4\text{AmO}, 2\text{HO} + 3\text{CphO}_6$ . The former compound is obtained when ammonia gas is led over the hydrate of camphoric acid; it crystallizes from the aqueous solution in fine needles. Acids separate the hydrate unchanged. *Lead, copper, and silver salt* are precipitated in the form of powder. We obtain the second combination by saturating a boiling solution of the hydrate of camphoric acid with bicarbonate of ammonia. It is separated in white prisms which give an acid reaction. *Potassa salt*,  $\text{KO}, \text{HO}, \text{CphO}_6$ , crystallizes in small six-sided needles. The combinations with the alkaline earths crystallize and are soluble in water. Lead, copper, and silver salt are insoluble.

*Camphorate of Orychloride of Acetyl:*  $2\text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} + \text{CphO}_6 \right.$ , is obtained by the action of chlorine upon camphorate of ethyl; taste bitter, not acid, odor agreeable, like *calycanthus*. In an alcoholic solution of potassa it separates into camphorate and acetate of potassa and chloride of calcium.

*Sulpho-camphoric Acid.*—If we dissolve anhydrous camphoric acid in fuming sulphuric acid, dilute the brown liquid with water, saturate with baryta, filter, and precipitate with sulphuric acid the baryta from the dissolved remainder of baryta salt, we thus obtain, after evaporating the solution, crystals of sulpho-camphoric acid, consisting of  $\text{C}_{18}\text{H}_{14}\text{S}_2\text{O}_{10}$ .

*Phoron.* *Phoron:*  $\text{C}_{18}\text{H}_{14}\text{O}_2 = 4$  volumes gas. If the camphorate of lime be subjected to dry distillation, we obtain a yellowish oil, lighter than water, odor like peppermint, boiling point  $202^\circ$ . It dissolves in sulphuric acid with a blood-red color. It is decomposed by the action of potassa-lime.

*Phtalinic Acid* (Phtalic Acid, Naphthalinic Acid, Phtalinic acid. *Alizarrinic Acid*):  $\text{C}_{16}\text{H}_4\text{O}_6 = (\text{C}_2\text{H}_2, \text{C}_{10}, \text{C}_2\text{H})\text{O}_3, (\text{C}_2\text{H})\text{O}_3 = \text{PhtO}_6$ , is formed by the action of nitric acid upon naphthaline, as well as by the action of dilute nitric acid, nitrate of peroxide of iron, and chloride of iron upon alizarin (see Dyestuffs). *Anhydrous phtalinic acid* is obtained by cautious sublimation of the hydrate.

Long, flexible, white needles, of silky lustre, insoluble in cold water, easily soluble in boiling; the hydrate is separated from the boiling solution; fuses at  $105^{\circ}$ , and burns with a luminous, sooty flame.

*Phtalamic Acid:*  $\text{NH}_4\text{O} + \text{NH}_2, \text{PhtO}_5$ . A hot alcoholic solution of phtalinic acid is saturated with ammonia, Phtalamic acid. small colorless prisms of phtalamate of ammonia are separated, which are easily soluble in water, and correspond to the above formula. If the solution of this salt be precipitated with acetate of lead, the precipitate treated with hydrosulphuric acid, and the fluid evaporated, we obtain phtalinate of ammonia. If to a boiling alcoholic solution of phtalamate of ammonia *nitrate of silver* be added, we obtain, after a few minutes, small needles of the phtalamate of silver; these are decomposed by boiling water, and small shining leaves are deposited  $= \text{AgO}, \text{C}_{16}\text{H}_7\text{N}_2\text{O}_3 = \text{AgO}, \text{NH}_3, \text{NH}, \text{C}_{16}\text{H}_3\text{O}_3$ . By heating phtalamate of ammonia, Phtalamid. we obtain *Phtalimid*  $= \text{NH}, \text{C}_{16}\text{H}_4\text{O}_4$ . This substance is tasteless, inodorous, fuses easily, sublimes unchanged, somewhat soluble in cold water, more easily in boiling water, and in alcohol. By boiling with alkalis, and concentrated acids, we obtain ammonia and phtalinic acid.

*Hydrate of Phtalinic Acid:*  $2\text{HO}, \text{PhtO}_6$ . We heat chlor-naphthalin with 4 to 5 parts nitric acid so long Hydrate of phtalinic acid. as the formation of nitrous acid is observed, and evaporate the mass upon the water-bath. The dry residue is dissolved in boiling water, and in cooling phtalinic acid separates in leaflets of mother-of-pearl lustre. If, with an excess of the *hydrate of lime*, the above hydrate be distilled, it separates into carbonic acid, and benzin ( $\text{C}_{12}\text{H}_5$ )H. By treating with *nitric acid*, we obtain nitro-phtalinic acid. The acid saturates 2 atoms base; the combinations with alkalis are soluble in water, those with alkaline earths are insoluble. The acid ammonia salt  $\text{NH}_4\text{O}, \text{HO}, \text{PhtO}_6$ , crystallizes in rhomboidal, or six-sided plates; it separates by distillation into water and *phtalimid*.

*Nitro-phtalinic Acid:*  $\text{C}_{16}\text{H}_3\text{O}_6, \text{NO}_4$ . The hydrate of nitro-phtalinic acid by cautious sublimation loses the water, and forms white needles an inch in length. The Nitro-phtalinic acid. hydrate,  $2\text{HO}, \text{C}_{16}\text{H}_3\text{O}_6, \text{NO}_4$ , is obtained by the action of nitric acid upon phtalinic acid—(see Naphthalin). It forms beautiful, pale, yellow crystals; easily soluble in boiling water, not easily soluble in cold, dissolves readily in alcohol and ether; decomposes by rapid heating with deposition of charcoal. The acid saturates 2 atoms base. The *ammonia salt* crystallizes in thin, colorless needles of mother-of-pearl lustre, easily soluble in water, and rather easily in alcohol. The compounds with the alkaline earths are insoluble. The acid gives with oxide of lead two salts, with 4 and 3 atoms base.

*Terephthalic Acid*:  $2\text{HO}, \text{C}_{16}\text{H}_4\text{O}_6$ . The resinous body, which is obtained by the action of nitric acid upon oil of turpentine (*see above*, Terecrylic Acid), is treated with boiling water, in which the terebenzinic acid is dissolved. From the residue we extract the terephthalic acid by ammonia, and purify the ammonia salt by crystallizing repeatedly, and boiling with animal charcoal. The acid is then precipitated by hydrochloric acid; a white, tasteless, crystalline powder, insoluble in water, alcohol, and ether. By heating, a part is sublimed unchanged, whilst the other part is decomposed by forming benzin. The salts are nearly all crystallizable and easily inflammable.

*Terebinic acid*. *Terebinic Acid*:  $\text{HO}, \text{C}_{14}\text{H}_9\text{O}_7$ , occurs in the acid solution, which is obtained by the action of nitric acid upon turpentine oil (*see Terecrylic Acid*). It is, for the removal of nitric acid, evaporated, and the residue dissolved in water. Out of the aqueous solution we obtain, by evaporation, the terebinic acid in crystals. It forms small, somewhat regular crystals, whose level sides possess an extraordinary lustre; taste pure and sharp acid. The acid saturates 1 atom base. The solution of terebinic acid gives no precipitate with *vinegar of lead*. In the same manner acetate of lead, chloride of calcium, and nitrate of silver are but slightly precipitated by the ammonia salt. Silver salt forms in beautiful, tufted crystals, of a silky lustre; undergoes a high temperature without decomposition.—

By distillation terebinic acid separates into *pyroterebinic acid*,  $\text{C}_{12}\text{H}_{10}\text{O}_4$ , and carbonic acid. Pyroterebinic acid forms a colorless, oily liquid; it has an odor like butyric acid, and a burning, etheric taste.

#### SALT-LIKE COMBINATIONS, CONSISTING OF THE OXIDES OF THE METHYL GROUP, WITH THE ACIDS OF THE SUCCYL GROUP.

*Combinations of oxide of methyl.* *Succinate of Methyl*:  $2\text{MeO} + \text{SuO}_6 = 4$  volumes gas. Into a hot solution of succinic acid in wood-spirit, hydrochloric acid gas is led, and, by admixture of water, the succinate of methyl is precipitated, which is washed a few times with water, then placed upon chloride of lime, and, finally, distilled. At ordinary temperature it is a solid crystalline mass, which fuses at  $20^\circ$ , and stiffens under  $16^\circ$ ; in water scarcely soluble, in alcohol and ether easily soluble. Boiling point  $198^\circ$ ; sp. gr. 1.1179. Sp. gr. of vapor 5.25.

*Suberate of Methyl*:  $2\text{MeO}, \text{SuO}_6$ . A colorless, liquid compound, of peculiar odor; boiling point  $240^\circ$ , sp. gr. 1.014. Brought in contact with ammonia it changes to a white crystalline mass.

*Combinations of oxide of ethyl.* *Succinate of Ethyl*:  $2\text{AeO}, \text{SuO}_6$ . A clear, colorless fluid, unctuous to the touch, sharp burning taste, and peculiar odor. Chlorine converts the compound first into the succinate of oxychloride of acetyl, and



then into the chlor-succinate of oxychloride of chlor-acetyl. Succinate of ethyl dissolves from six to ten per cent. of pure oxide of lead. If the solution be heated there are formed water, alcohol, and probably an acid, consisting of  $C_8H_3O_5$ . Potassium and sodium act violently upon ether, forming  $AeO, C_8H_3O_5$ .

*Suberate of Ethyl*: Very thin-flowing, colorless, odor feeble, burning, irritating taste; soluble in alcohol and ether in all proportions. If ammonia gas be led into the etheric solution, a slightly crystalline deposit is formed; sp. gr. 1.003, boiling point  $260^\circ$ .

*Adipinate of Ethyl*:  $2AeO, AdO_6$ , possesses an apple-like odor, boils at  $230^\circ$ , sp. gr. 1.001. By chlorine it is changed into a resinous mass.

*Sebacylate of Ethyl*:  $2AeO + SeO_6$ . An oily, colorless fluid, of a pleasant, melon odor; solid at  $-9^\circ$ , and crystalline; boils above  $100^\circ$ , lighter than water.

*Camphorate of Ethyl*:  $2AeO + CphO_6$ . Ether-camphoric acid separates by distillation into anhydrous camphoric acid and camphorate of ethyl. A liquid of oily consistency, somewhat darkly colored, of unpleasant, bitter taste; when poured upon paper the odor is nauseous and insupportable; not inflammable at ordinary temperature, easily soluble in alcohol and ether, capable of distillation. Chlorine converts the compound into camphorate of oxychloride of acetyl.

*Ether-camphoric Acid*:  $AeO, HO, CphO_6$ , is obtained when ten parts camphoric acid, twenty parts alcohol, and five parts sulphuric acid are boiled until one-half the quantity is distilled over. From the residue the ether-camphoric acid is precipitated by water, washed a few times with water, dissolved in potassa, and precipitated from the solution by hydrochloric acid. At ordinary temperature, of molasses consistency, transparent, colorless, of feeble odor, and bitter, unpleasant, not acid taste; slightly soluble in water, easily in alcohol and ether. It forms with the bases salts, soluble and insoluble. Copper salt, which is obtained by the admixture of the ammonia salt with sulphate of copper, consists of  $2CuO + 3AeO + 3CphO_6$ .

*Phtalinate of Ethyl*:  $2AeO, PhtO_6$ , appears in the form of an oily liquid.

### *Second Group.*

#### CARBON NUCLEUS: $C_4$ .

Glycyl:  $Gl=C_2, H_2, C_4, H=C_6H_5(?)$ .

Like spermaceti and the different waxes, most of the fats which occur in nature, solid as well as fluid, are combinations of an organic base called oxide of glycyl with the so-named fatty acids belonging to the formyl series, and the fatty acids of the oleyl group.



Yet these bases are not hitherto known isolated. If, for instance, we boil the different fats with potassa, the fatty acids combine with the potassa to form soap, whilst a sweet-tasting body is separated called *glycerin*, consisting of  $C_6H_8O_6$ . In accordance with its constitution, this body evidently cannot be the base of fats, as is also established by the results of analyses. Thence it follows that this base probably consists of  $C_6H_3O$ . (According to others of  $C_3H_2O$ .) Hence glycerin is formed when the constituents of 5 atoms water unite with oxide of glycyll,  $C_6H_3O + 5H_2O = C_6H_8O_6$ . Glycerin is not a simple oxide, for in that case it must be an acid, but it is an indifferent body, which in many respects agrees with *mannit*, and is with it described. If we subject glycerin to dry distillation, we obtain *acrolein*,  $HO, C_6H_3O$ , but neither is this body the base of fats; hence the elements in the two materials must be differently united. If we accept for acrolein the formula  $HO, (C_2, C_4H_3)O$ , or  $HO, (C_4H_2, C_2H)O$ , and for oxide of glycyll ( $C_2H_2, C_4H$ ), their difference is explained.

We have already seen in *propion* (page 148), that, according to new investigations, it is a mixture of different substances, consisting of an organic oxide with the oxyhydrates of the formyl series. This oxide consists of  $C_{12}H_9O$ . If, for instance, we boil the so-called propion with a solution of potassa, there goes over an easily mobile, colorless liquid, which when inspired produces the effect of chloroform and ether in the highest degree, and consists of  $C_{12}H_9O_5, HO$ . This oxide may be considered as consisting of  $(4 C_2H_2, C_4H)O$ , and therefore represents the fourth member in the group with the nucleus  $C_4$ .

#### COMPOUNDS OF THE OXIDE OF GLYCYL—FATS AND OILS.

As remarked above, the fats can be viewed as combinations of oxide of glycyll, with the different fatty acids; hence they rank amongst the compounds of the oxides of the methyl group, with the acids of the formyl series. Yet most of the fats which occur in nature are mixtures of different fats. The pure combinations, whose perfect exhibition is often impossible, assume the name of the acid, with the termination *in*.

Thus, by stearin, we understand the stearinate of glycyll; by margarin, the margarate of glycyll. If the acid be solid, so also is the combination with oxide of glycyll, only the melting point of the latter is about  $15^\circ$  lower than that of the corresponding acid hydrate. The fluid, fatty acids give, with oxide of glycyll, at ordinary temperature, fluid fats, or oils, which are essentially distinguished from the solid fats by their easy solubility in cold alcohol.

*Butyrin*, or *butyrate of glycyll*, is not known in the pure state. Mixed with capronin, caprin, caprinin, and olein, we obtain it

from butter, when we agitate it with cold alcohol, and evaporate the solution (*see* Butyric Acid). This mixture appears as a pale-yellow oil, which stiffens at  $0^{\circ}$ , and possesses distinctly the smell of warm butter.

*Valerianate of Glycyl*.—Neither can this substance be exhibited in a pure state; it occurs in fish-oil.

*Laurostearinate of Glycyl* (Laurin, Laurostearin), is obtained by boiling pulverized laurel-berries with alcohol; it is deposited in cooling, and is obtained pure by alternately washing with cold alcohol, and crystallizing out of boiling alcohol; crystallizes in white, loose needles, which are easily soluble in boiling alcohol and ether; fuses at  $44^{\circ}$ .

*Myristicinate of Glycyl* (Myristicin). When oil of nutmeg is extracted, by alcohol, the above compound remains behind; crystallizes out of boiling ether, in needles of silky lustre, soluble in boiling ether in all proportions; fuses at  $31^{\circ}$ .

*Palmitinate of Glycyl* (Palmitin), occurs in palm-oil, and Japanese wax. Repeatedly crystallized from ether, it appears in small crystals; fusible at  $60^{\circ}$ ; almost insoluble in alcohol, easily soluble in boiling ether.

*Margarinate of Glycyl* (Margarin). We extract tallow, containing margarin, with cold ether, until it no longer loses weight. From the etheric solution margarin is first separated by spontaneous evaporation, and, by being pressed between filter-paper, is freed from adhering olein. Melts at  $48^{\circ}$ ; dissolves in 10 parts ether. If we subject olive-oil to a lower temperature, we obtain a combination of margarin and olein, which melts at  $20^{\circ}$ .

*Stearinate of Glycyl* (Stearin). This compound remains behind, when mutton tallow is washed with ether, until it suffers no more loss; it separates from the boiling, alcoholic solution in flakes; fuses at  $62^{\circ}$ , and stiffens to a crystalline, transparent, easily friable mass; abundantly soluble in boiling ether, but, in cooling, it is again completely separated.

*Stearophanate of Glycyl* (Stearophanin), occurs in the *coccus Indicus*. Forms, from the etheric solution, tooth-like, crystal groups; fuses at  $36^{\circ}$ .

*Oleinate of Glycyl* (Olein), is unknown in the pure state. Mixed with margarin, we obtain it when olive oil is agitated with alcohol, and the solution slowly evaporated; at first, margarin is separated, and, finally, a mixture remains of olein and margarin, which we treat a few times in the same way. It is then destitute of color, taste, and smell; easily soluble in cold alcohol; stiffens at a low temperature.

*Elaidinate of Glycyl* (Elaidin). If into olein (or olive oil?) we lead nitrous or sulphurous acid, it stiffens, forming elaidin, which is then strongly compressed between paper; is dazzling white; melts at  $36^{\circ}$ ; easily soluble in ether, nearly insoluble in

alcohol ; appears like stearin. *Palmin* we obtain by leading nitrous acid into ricinus oil ; completely white, fracture wax-like ; fuses at  $66^{\circ}$  ; easily soluble in boiling alcohol and ether.

*Fats occurring in Nature.*

The fats occurring in nature can be divided into *general* and *special*. The former occur in almost all plants, and parts of plants ; the latter belong only to certain vegetable matters (Laurostearin, myristicin, palmitin).

The consistence of the general fats is determined by the proportions of margarin, stearin, and olein. In the solid fats (butter, suet, tallow), the former predominates ; in the fluids, or oils, the latter. According as the oils contain oleinic or olinic acid, they are called *greasy*, or *dry* ; to the former belong olive oil, almond oil, hazel-nut oil, beech-nut oil, rape-seed oil, etc. To the latter linseed oil, nut oil, hemp oil, poppy oil, grape-seed oil, etc. They are used for varnishes.

Occurrence of fat. In the *vegetable kingdom*, the fats occur mainly in the seeds, and especially in the seed lobes, seldom in the perisperm (poppy), or in the fleshy matter surrounding the seeds (olive). In the seeds, the fat is mostly inclosed in cells, together with a protein compound. In the *animal kingdom*, certain parts of the body are entirely occupied with fat-cells, as directly under the skin (*paniculus adiposus*), in the cavity of the abdomen, in the so-called omentum, around the kidneys, in the tubular cavity of the bones. Fat also occurs in milk (fat globules), inclosed in cells.

Formation of fat in animal body. No doubt exists that a great portion of the fats found in the animal body originate in the vegetable kingdom, since they generally occur with the proteine compounds in the body ; a part, as we conclude from numerous observations, are formed like wax in the animal organism, and in most cases it is without doubt the non-nitrogenous nutriment, particularly amyllum, which, by a process of deoxidation, serves for the formation of fat ; yet, in the animal body, fat appears only to be formed when matter containing amyllum in common with fat, enters the body.

Production of fats. If the fat in the animal body is contained in cells, its separation consists simply in bringing these cells, divided, into hot water. The cells burst, and the fat collects upon the surface of the water. If fat be contained in abundance in vegetable matter, as in seeds, it is obtained by expression. The dried seeds are ground and compressed between either cold or warm metal plates. *Olives*, before being pressed, are laid in heaps ; they commence to ferment, and can be then entirely expressed. If portions of vegetable and animal matter contain fat only, it may be extracted by ether.



In a pure state, most of the fats are odorless and tasteless. When they possess an odor it is generally owing to small quantities of volatile fat acids, as butyric acid, capronic acid, etc., which become free by decomposition of a part of the oxide of glyceryl compounds. This is consequent upon the presence of water and air, by a kind of fermentation, and apparently it depends upon the presence of a nitrogenous substance.

Properties of  
fats.

Fats are insoluble in water; in cold alcohol, with the exception of ricinus oil, they are soluble only in small quantity, yet they are absorbed the more abundantly the more olein they contain. They are dissolved by boiling alcohol, but in cooling the greater portion of them again separate, particularly the fats containing stearin. All fats are extracted by ether, those containing stearin in least quantity; the sp. gr. varies from 0.91 to 0.93.

By heating, the fats assume a darker color, and boil between 250 and 300°; but the boiling point continually ascends, owing to constant decomposition. From oxide of glyceryl arises acrolein; oleic acid leaves sebacic acid, and from the products of the distillation of fats containing margarin and stearin, margaric acid arises, at the same time hydrocarbon is formed. Quickly exposed to a higher temperature, they are completely decomposed. (Oil gas.)

In closed vessels the pure fats suffer no change; exposed in thin layers to the air, those containing olein and olin quickly absorb oxygen, under powerful evolution of heat, which may increase even to the inflaming of porous bodies (cotton). The purer fats are, the quicker oxidation takes place. If the fats contain slimy matter, it can be removed by heating with oxide of lead and water (use in preparation of varnish). The action of nitric acid, nitrous acid, chlorine, sulphuric acid, etc., upon the fats, is the same as upon the fatty acids. In the heat, the fatty oils dissolve sulphur, a part of which again separates in cooling. If we heat sulphur with the fats, the same phenomenon appears which was mentioned in connection with odmyl. (*Vide* page 80.)

### *Soaps and Plasters.*

The common soaps are mixtures of stearate, margarate, and oleate of potassa or soda, which are obtained when the ordinary fats of the animal and vegetable kingdom are decomposed by potassa or soda. The remaining salts of the fat acids, which are distinguished from those of the alkalies by their insolubility in water, are not generally included with the soaps; thus the insoluble oxide-of-lead soap is called lead plaster. There are combinations with the fatty acids, which they class with the alkalies; hence, what properties a mixture of these combinations must possess, is evident from a study of the same.

Soaps.



Hard and soft  
soap proper-  
ties.

There are *hard* and *soft soaps* to be distinguished, as well as *soda* and *potassa* soaps. *Potassa* generally gives softer compounds than *soda*. The hardest compound is the stearate of soda, the softest the oleinate and olinatate of potassa. If stearate and margarate of soda contain water, they lose it entirely by being exposed to the air; they dissolve in water without swelling to a gelatinous mass. If completely dry oleate of potassa be exposed to damp air, the former absorbs water, and doubles its weight. If it be placed in three times its quantity of water, it swells to a transparent jelly, which, upon addition of more water, exhibits a stringy, syrup-like mass. Hence it follows that fats rich in stearine and margarine must give hard soaps, those containing olein and olin soft soaps. The drying oils generally contain but little margarin. Linseed oil, nut oil, hemp oil, etc., are hence used especially for the manufacture of softer soaps. Olive oil contains much margarin, and hence it gives rather a hard soap. The stearates and margarates of alkalis differ widely from the corresponding oleic and olic acid compounds, in their behavior to alcohol. The latter dissolve easily in cold alcohol; the former, on the contrary, are only slightly soluble in cold alcohol; and if the hot saturated solution be cooled, the entire mass congeals to a hard jelly, at first transparent, but after a little becomes opaque, by forming shining crystals (spirits of soap and opodeldoc). The stearate, margarate, and oleate of the alkalis, as also the mixtures of the same (the soaps), dissolve completely in not too great a quantity of water, and by farther addition of water are separated into free alkalis and acid salts. But the dissolving of soap does not take place in a solution of common salt, of pure potassa, or the carbonate. On the contrary, an aqueous solution of soap possesses the property of withdrawing water from a solution of those substances, when the latter is not too concentrated, and of going over into a gelatinous state. If common salt be added to a solution of soda soap, the soap is separated; but this separation does not take place if chloride of potassium be used instead of common salt. If the solution of common salt be diluted, the separated soap retains a quantity of water; it is thence soft, greasy, and gelatinous. If the separated watery soap be warmed with a saturated solution of common salt, the soap yields up its water, and becomes more solid. Hence, if a dilute solution of common salt be boiled a long time with the soap, in proportion as the solution is concentrated by evaporation, the soap will absorb water. If the salt solution be so concentrated that it can draw no more water from the soap, then the soap has also no longer the property to absorb water from the salt solution. The soap is then separated; after cooling it is of harder consistency, and is called *essential soap*. If common salt be added to a solution of potassa soap, we obtain chloride of potassium

and soda soap; but since chloride of potassium does not effect the separation of the soap, if an excess of salt has not been used in this decomposition, a farther addition of salt is necessary.

In order to saponify fat, strictly speaking, only so much alkali is necessary as the acids occurring in the same require for their neutralization; yet an excess of alkali is always used, in order completely to divide the soap from the water. If less alkali be taken than is necessary to form neutral salts with the fatty acid, the excess of fat combines with the formed, fatty-acid salts, not, indeed, chemically, but yet so intimately that the whole exhibits an emulsion-like mass, called soap-lime. If this soap-lime be treated with potash lye, it soon forms a transparent mass, which may be drawn out into threads; if now to the mass common salt be gradually added, in proportion as the salt dissolves, the soap separates, whilst the glycerin, and the excess of alkali, remain in the aqueous solution. The process of saponifying is commenced by a weak alkaline solution, and the soap-lime, thereby obtained, is led over into soap by the addition of stronger lye, which soap is then completely separated by common salt.

Soaps are used in washing, in fulling cloths, and in medicine. The use in washing depends upon two considerations: First, upon their power of taking fatty matters from cloths, and therewith forming an emulsion-like mass, soluble in water. Secondly, upon the ease with which the neutral, fatty, acid salts, by much water, separate into acid compounds and free alkali. The latter acts upon the uncleanness of the stuffs, and forms therewith compounds, in part soluble, in part such as no longer cleave to the cloth, whilst the separated fatty acid salt preserves the smoothness of the surface of the cloth.

The combinations of the fatty acids with the alkali line earths, earths, and metal oxides are insoluble in water. If a solution of soap be mixed with a salt of the above-mentioned bases, a precipitate is formed. Water, which contains much earthy salts in solution, can, hence, not be used in washing, because the fatty acids form with the earths insoluble soaps, which are deposited upon the cloth, to which they cleave so closely that they cannot be washed away. Since the earthy salts found in water are mostly held in solution by carbonic acids, such hard water can be improved by boiling.

If to a solution of soap a solution of sugar of lead be added, a white, plaster-like precipitate is formed, which, after due washing, exhibits a brittle, pulverizable mass, which, when heated, becomes soft, and can be drawn out into long threads. A like combination is obtained, when 5 parts very finely rubbed oxide of lead are digested several hours upon the

water-bath with 9 parts sweet-oil, or suet, with constant stirring, and the addition of a little water.

### *Third Group.*

Carbon Nucleus:  $C_6$ .

The third group of the Hydropolycarbyls, with the nucleus  $C_6$ , embraces:—

- a. *The Nicid Group*, and
- b. *The Niceyl Group*.

### THE NICID GROUP.

Component  $C_2H_2$ ; Nucleus  $C_6$ ; Active element H.

Of this group only the second member is, as yet, known; and, indeed, of that, only the chlorine combination.

*Chloride of Nicid*:  $NcCl = (2C_2H_2, C_6, H)Cl = C_{10}H_5Cl$ . This combination is obtained, when chlorniceinic acid is distilled with an excess of lime or baryta. It separates into chloride of nicid, benzin, and paranicen, which sublime as hard, lemon-colored bodies. Chloride of nicid and benzin are separated by fractional distillation. A fluid, pale, amber color; sp. gr. 1.141; boiling point  $242^\circ$ . Gives, with fuming nitric acid, nitrochlornicid  $C_{10}H_4NO_4Cl$ , which crystallizes in long, yellow needles of silky lustre. If the nitro-combination be treated with ammonia and hydrosulphuric acid, we obtain the organic base *Chloronicin*,  $C_{10}H_6ClN$ .

*Paranicin* is a lemon-colored body, of penetrating smell and taste; crystallizes in broad leaves; is soluble in alcohol and ether, is sublimable, and consists of  $C_{20}H_{12} = 4$  volumes gas; gives, with nitric acid, a nitro-combination, and, with hydrosulphuric acid and ammonia, the base *paranicin*. Hence, *paranicin* consists of  $(5C_2H_2, C_{10}, H)H$ .

### THE NICEYL GROUP.

Component  $C_2H_2$ ; Nucleus  $C_6$ ; Active part  $C_2H$ .

To this group belong:—

Member 2. Niceyl,  $Ne = 2C_2H_2, C_6, C_2H = C_{12}H_5$ .

“ 3. Terebencyl,  $Tr = 3C_2H_2, C_6, C_2H = C_{14}H_7$ .

*Chloroniceinic acid*. *Chloroniceinic Acid*:  $2HO + (C_2Cl_2, C_2H_2, C_6, C_2H)O_3 + (C_{12}H_5)O_3 = HO, C_{12}H_4ClO_3$ . This double acid is obtained, if into a solution of 60 grms. benzoic acid, and 200 grms. hydrate of potassa in 300 grms. water, chlorine gas be led so long as carbonic acid is evolved. A gray, crystalline precipitate is

formed, which consists of chlorate of potassa and chloroniceinate of potassa, whilst in the solution benzoate of potassa and chloride of potassium occur. The mass is diluted with half its volume of water saturated with hydrochloric acid, and then boiled. The chloroniceinic acid is separated as an oily fluid, which stiffens after cooling, and, by frequent treatment with boiling water, and repeated crystallization with alcohol, is purified. Crystallizes in groups of microscopic crystals, in the form of a cauliflower; fuses at  $150^{\circ}$ ; boils at  $215^{\circ}$ ; is sublimable.

*Ammonia salt* crystallizes in broad glimmering leaves, melts, and is volatile undecomposed; loses ammonia in the light, and becomes acid. If we mix an alcoholic solution of chloroniceinate of ethyl with ammonia, we obtain *chloronicein-amid*, in large, fatty lusted leaves. The *baryta salt* appears as a white crystalline powder; little soluble in water, easily soluble in hot alcohol. The *silver salt* is a white crystalline powder.

The *oxide of ethyl compound* is a colorless fluid; sp. gr. 0.981; boils at  $230^{\circ}$ . With *nitric acid*, chloroniceinic acid gives *nitro-chloroniceinic acid* =  $(C_2Cl_2, C_2 2(NO_4), C_6, C_2H) + (C_{12}H_5)_2O_3 = (C_{12}H_3Cl, NO_4)_2O_3$ . With *fuming sulphuric acid*, we obtain a *paired acid*.

*Terebenzinic Acid*:  $HO_2(C_{14}H_7)_2O_3$ , is formed by the action of nitric acid upon turpentine oil (*vide* Terebenzinic acid. Terephthalic Acid, page 184). It separates from the hot aqueous solution in white shining needles; fuses at  $169^{\circ}$ ; sublimes in an open vessel, even under  $100^{\circ}$ . The salts agree in solubility with those of benzoic acid. The *oxide of ethyl compound* smells like anise, and boils at  $130^{\circ}$ .

#### PAIRED COMBINATIONS OF THESE GROUPS.

a. Pairling  $C_2HO_2$ ; Component  $C_2H_2$ ; Nucleus  $C_6$ ; Active element H.

*Furfurol*:  $C_2H, \wedge (C_2H_2, C_6, H)O_4 = C_2H, O_2, \wedge (C_2H_2, C_6, H)O_2 = C_{10}H_4O_4$ . Furfurol (artificial formic oil) is formed by the action of sulphuric acid upon wheat-bran, wheat-meal, and sawdust. Pure amylum, pure gums, and cellulose, do not furnish this body. We distil a mixture of 2 parts wheat-bran, and 1 part sulphuric acid, which is mingled with the same volume of water. The obtained acid distillate is saturated with potassa, and is then again subjected to distillation, until one-fifth has gone over. The distillate is then rectified over chloride of calcium. A colorless transparent fluid, of pleasant aromatic taste, and smell; burns with strong, sooty, luminous flame; boils at  $162^{\circ}$ ; sp. gr. 1.1641 at  $15^{\circ}$ . *Furfurol* dissolves in 12 parts water; is easily soluble in alcohol and ether; after a short time becomes dark colored and forms a resinous substance; *chlorine* and *bromine* change it into



resinous products; *nitric acid* decomposes it, forming *oxalic acid*. It dissolves in concentrated sulphuric acid, with splendid red color. Addition of water causes it again to separate.

*Sulpho-furfurol*:  $(C_{10}H_4) \left\{ \begin{array}{l} S_2 = C_2H, O_2 \\ O_2 \end{array} \right. (C_2H_2, C_6, H)S_2$ , is obtained, when hydrosulphuric acid is led into an alcoholic solution of furfurol. It is precipitated as a white crystalline powder; is decomposed by dry distillation, forming colorless crystalline needles; consisting of  $C_{18}H_8O_4$ ; in water it is scarcely soluble, but dissolves easily in alcohol and ether.

*Nitrofurfurol*:  $3C_{10}H_4O_2 + 2N$ . It is formed, when furfurol is brought in contact with aqueous ammonia. Separates from the hot saturated alcoholic solution in tufts of thin short needles. Pale-yellow, odorless; insoluble in cold water, soluble in alcohol and ether. Treated a short time with hot water, or with hydrochloric acid, it separates into furfurol and ammonia. Boiled with a dilute solution of potassa, it changes into the organic base *furfurin*:  $= N_2C_{30}H_{12}O_6$ .

b. Pairling  $C_2HO_2$ ; Component  $C_3H_2$ ; Nucleus  $C_6$ ; Active part  $C_2H$ .

*Chinon*:  $C_2H, O_2 (C_2H_2, C_6, C_2H)O_2 = C_{12}H_4O_4$ . Chinon is obtained when chinic acid, or a chinic acid salt, is warmed with 4 parts manganese, 1 part sulphuric acid, and 1 part water. Chinon escapes in thick vapor, which condenses on the sides of the cooled receiver in fine gold-colored needles; purified by repeated sublimation. Needles, often an inch in length, form, which easily melt, and stiffens to a crystalline mass; in cold water not easily soluble, easily so in boiling water, alcohol, and ether. The solution colors the skin lastingly brown, sublimes even at common temperature; its gas diffuses a strong, tear-exciting odor, and leaves behind an action similar to chlorine and bromine. The aqueous solution of chinon gradually grows dark-colored, by the formation of a humin-like substance. It is led over by chlorine into several secondary combinations.

If we lead a current of ammonia gas into a tube filled with chinon, we thus obtain *chinon-amid*,  $NH_2, C_{12}H_4O_3$ , as an emerald crystalline mass. If a solution of chinon be mixed with a solution of caustic potash, we thus obtain, by absorption of oxygen upon the addition of an acid, a black mass—the so-called *chinonic acid*.

*Colorless Hydrochinon*:  $C_{12}H_6O_4 = C_{12}H_4O_4 + H_2$ , is formed by the dry distillation of chinic acid, as also by leading *iodide* of hydrogen into a concentrated solution of chinon. After dilution, hydro-chinon remains behind. It appears in regular six-sided transparent prisms, colorless and inodorous, sweet tasting, not acid; easily soluble in water and alcohol; sublimes like benzoic acid. If it be quickly heated

Combinations  
of chinon.

above its sublimation point, it separates into chinon and green hydrochinon.

*Green Hydrochinon*:  $C_{12}H_5O_4 = C_{12}H_4O_4 + H$ . If to a solution of the preceding combination a solution of chinon be added, immediately green crystals form; these will also be obtained, if the colorless compound be brought in contact with a solution of *perchloride* of iron, chlorine, nitric acid, nitrate of silver, or chromate of potassa; appears in thin, often very long crystals, which possess the green metallic lustre of the Spanish fly. Pungent taste, feeble chinon-like odor; melts easily; little soluble in cold water, but easily so in alcohol and ether; boiled with water, it separates into chinon and colorless hydrochinon.

*Hydrochlorate of Hydrochinon*:  $C_{12}H_6O_4 + HCl$ . From the solution of chinon in concentrated hydrochloric acid, by gentle evaporation, the hydrochloric acid compound is separated in colorless prisms, united in ray forms. Odor peculiar, taste sweet and burning; fuses easily, and dissolves readily in water, alcohol, and ether. If a solution of this compound be mixed with nitrate of silver, metallic silver is separated, together with formation of chinon. It dissolves in pure ammonia, with a deep blue color.

*Brown Sulphohydrochinon*:  $C_{12}H_5O_4S_2$ , is obtained simultaneously with green hydrochinon by leading hydrosulphuric acid into a solution of chinon. It is precipitated as a dark brown, powdery, amorphous substance, destitute of taste and smell; melts readily, and is easily soluble in alcohol.

*Yellow Sulphohydrochinon*:  $C_{12}H_6O_4S$ , is formed, when the preceding combination, diffused in water, is subjected to the continued action of hydrosulphuric acid. Or, we saturate an alcoholic solution of chinon with hydrosulphuric acid, filtrate away from the separated sulphur, and dilute the yellow, alcoholic solution. A yellow powder, soluble in alcohol, ether, and acetic acid; from the hot aqueous solution the greater part is again separated in cooling. It fuses even below  $100^\circ$  under partial decomposition. If we mix the alcoholic solution with a solution of chinon, brown sulphohydrochinon is at once separated, with a simultaneous formation of colorless and green hydrochinon.

*Rhomboidal Sulphohydrate of Hydrochinon*:  $3C_{12}H_6O_4 + 2HS$ . If into a cold saturated solution of colorless hydrochinon, hydrosulphuric acid be led, small shining crystals are separated, which, by being warmed, whilst gas is constantly introduced, again dissolve. By being slowly cooled, the compound is separated in colorless rhomboids, which must be quickly dried in vacuum. It is odorless. In contact with water it decomposes into hydrosulphuric acid and colorless hydrochinon. If hydrosulphuric acid be led into a solution of colorless hydrochinon, warmed to  $40^\circ$ , very long colorless prisms are obtained  $= 2C_{12}H_6O_4 + HS$ . Probably another combination exists  $= C_{12}H_6O_4 + HS$ .

Derived combinations of chinon.

If chinic acid with a chlor-mixture (one part chinic acid with four parts of a mixture consisting of two parts manganese, three parts common salt, and four parts sulphuric acid, admixed with three times the volume of water) be subjected to distillation, we obtain, in addition to the formation of formic acid, an oily body, and the evolution of carbonic acid gas, also a yellow crystalline sublimate, which is a mixture of *chlorchinon*, *bichlorchinon*, *trichlorchinon*, and *tetrachlorchinon* (chloranil). The chloranil not easily volatile can be readily condensed by gradually cooling the upper end of the conduction-tube, and become separated from the remaining products. These products are collected on a filter, washed with cold water, and dried. The dried mass is then digested a few times with small quantities of cold alcohol, so long as the latter is deeply colored; in the solution chlorchinon and terchlorchinon are found, whilst bichlorchinon remains mingled with small quantities of terchlorchinon and tetrachlorchinon. From the alcoholic solution trichlorchinon is first separated, and then chlorchinon. All these compounds like chinon unite with hydrogen.

*Chlorchinon*:  $C_{12}H_3ClO_4 = C_{12}H_4O_4 + C_2H(C_2Cl_2, C_6, C_2H)O_4$ . Crystallizes in tender yellow needles, melts at  $100^\circ$ , odor aromatic, taste sharp and burning, colors organic bodies purple; easily soluble in anhydrous alcohol and ether; forms, with concentrated sulphuric acid, a solution which after a little time stiffens to a soft mass of prisms. Combines with one and with two atoms of hydrogen, forming colorless and brown chlor-hydrochinon =  $C_{12}H_5ClO_4$  and  $C_{12}H_4ClO_4$ .

*Bichlorchinon*.

*Bichlorchinon*:  $C_{12}H_2Cl_2O_4 = C_2H, O_2(C_2Cl_2, C_6, C_2H)O_2$ . From the alcoholic solution it crystallizes in lemon-colored, glassy crystals, which fuse at  $150^\circ$ ; insoluble in water and in cold alcohol, easily soluble in boiling alcohol and in ether. If we heat bichlorchinon with concentrated aqueous sulphurous acid, we obtain by cooling star-formed groups of needles, of colorless *bichlorhydrochinon* =  $C_{12}H_4Cl_2O_4$ , which dissolve easily in hot water, in alcohol and ether. If we add perchloride of iron to the hot solution, we again obtain bichlorchinon. Indeed, if perchloride of iron be dropped in only so long as to darken the color of the solution, small violet prisms are separated, which are also obtained by mixing a solution of colorless bichlorhydrochinon in weak alcohol, with nitrate of silver. This compound is the *violet bichlorhydrochinon*, and consists of  $C_{12}H_3Cl_2O_4 + 2HO$ . If this compound be left to stand over concentrated sulphuric acid, by loss of water it goes over into *yellow bichlorhydrochinon*,  $C_{12}H_3Cl_2O_4$ .

*Terchlorchinon*.

*Terchlorchinon*:  $C_{12}HCl_3O_4 = C_2H, O_2(C_2Cl_2, C_6, C_2Cl)O_2$ . It separates from the warm alcoholic solution, when slowly cooling, in large yellow leaves. It is also obtained



by the direct action of chlorine upon chinon. Trichlorchinon fuses at  $160^{\circ}$ , but sublimes even above  $130^{\circ}$ . Insoluble in cold water, not easily soluble in cold alcohol, but easily in boiling alcohol and ether. It dissolves in warm aqueous sulphuric acid, and in cooling the colorless trichlorhydrochinon separates in colorless leaves. If to the solution of colorless trichlorhydrochinon in weak alcohol, nitrate of silver or perchloride of iron be added, in cooling small yellow leaves are separated.

*Tetrachlorchinon* (Chloranil):  $C_{12}Cl_4O_4 = C_2Cl, O_2 \wedge$  Chloranil.  $(C_2Cl_2, C_6, C_2Cl)O_2$ . Chloranil is produced not only by the action of chlorine upon chinic acid, but also in the complete decomposition of chlorisatin by chlorine, and the action of hydrochloric acid and chlorate of potassa upon anilin phenol, salicylous and salicylic acid, chinon, salicin, etc. It is most easily obtained when salicin and chlorate of potassa are dissolved in hot water, and hydrochloric acid is gradually added to the solution in small portions. After a few moments there is, together with abundant evolution of carbonic acid, a lively reaction, in consequence of which the surface of the fluid is covered with a thick layer of small sulphur-colored crystals of chloranil; appears in scales of metallic mother-of pearl lustre. Heated slowly, it sublimes without melting. Insoluble in water, entirely so in cold alcohol, dissolves in boiling alcohol, with pale-yellow color, but separates whilst cooling in shining iridescent leaves. Is not attacked by either nitric, sulphuric, or hydrochloric acid. Quickly heated, it melts into a dark brown fluid, boils, and suffers a partial decomposition. Boiled with aqueous *sulphurous acid*, it forms *Chlorhydroanil*,  $C_{12}H_2Cl_4O_4$ , which crystallizes in white leaflets, which become yellow when brought in contact with perchloride of iron or nitrate of silver.

If chloranil be dissolved in a warm dilute solution of potassa, it undergoes a transposition, whereby brownish, purple-red, shining prisms are separated from the purple-red solution, which prisms are chloranilate of potassa; in the solution chloride of potassium occurs  $= C_{12}O_4Cl_4 + 2KO = 2(C_6O_3Cl) + 2KCl$ .

*Hydrate of Chloranilic Acid*:  $HO, (C_6Cl)O_3$ . We Chloranilic acid. add to the aqueous solution of the chloranilate of potassa, an excess of hydrochloric acid, or sulphuric acid, and warm the liquid; whilst cooling, the chloranilic acid is separated, either in vermilion, crystalline kernels, or in narrow, reddish-yellow leaflets of bright, half-metallic lustre, according to the rapidity of the cooling. The acid dissolves in pure water with beautiful violet color. Hydrochloric or sulphuric acid immediately separates the acid again. By heating, the acid sublimes with partial decomposition. The *potassa salt* crystallizes in shining reddish purple crystals, in the same manner as the *ammonia salt*. Both dissolve in water with reddish-purple color.

*Chloranilamid*:  $NH_2, \wedge (C_6Cl)O_3$ . If chloranil be slightly warmed



with alcohol and ammonia, a part is dissolved with reddish-brown color, whilst chloranilamid remains undissolved. This substance is dissolved in warm alcohol, containing a little hydrate of potassa, and to the yet warm filtrated solution just so much hydrochloric acid is added as is necessary to the saturation of the potassa, by which means the chloranilamid is precipitated as a crimson crystalline powder. Insoluble in water, and nearly so in alcohol and ether. Warmed with an alcoholic solution of potassa, it separates into ammonia and chloranilic acid.

*Hydrate of Chloranilamidic Acid* (Chloranilam): Chloranilam.  $\text{HO}, (\text{NH}_2, \text{C}_6\text{Cl}, \text{O}_2) \text{---} (\text{C}_6\text{Cl}) \text{O}_3$ . We dissolve chloranil in ammonia, and over-saturate the cold solution with hydrochloric acid. The chloranilamidic acid is separated in small hairlike crystals, which, by repeated crystallization from the hot aqueous solution, are obtained in large crystals. If the crystals be pounded, we obtain a dark violet powder. Soluble in water and alcohol with violet color. Acids decompose the compound when heated—separating a brownish powder. A solution of potassa decomposes the compound into ammonia and chloranilic acid.

The *ammonia salt* (chloranil-ammon) is obtained, when chloranil is dissolved in warm aqueous ammonia.

By cooling, and cautiously evaporating, small flat needles form, of chestnut color and rather bright lustre. The salt dissolves in water, with reddish-purple color. From the diluted solution acids cause no precipitate; from the concentrated, chloranilamidic acid is precipitated. If the salt be mixed with an acid, we obtain chloranilic acid. Potassa evolves ammonia after a long time.

*Nitrate of silver* gives, with the ammonia salt, a very voluminous reddish-brown precipitate, which contains 4 atoms of oxide of silver to 1 atom of acid.

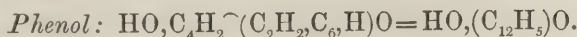
c. Pairling  $\text{C}_4\text{H}_2$ ; Component  $\text{C}_2\text{H}_2$ ; Nucleus  $\text{C}_6$ ; Active element H.

Here belong:—

The radical of Phenol	$\text{C}_4\text{H}_2, \text{---} (\text{C}_2\text{H}_2, \text{C}_6, \text{H}) = \text{C}_{12}\text{H}_5$ .
“ “ “ Creosote	$\text{C}_4\text{H}_2, \text{---} (2\text{C}_2\text{H}_2, \text{C}_6, \text{H}) = \text{C}_{14}\text{H}_7$ .
“ “ “ Carvacrol	$\text{C}_4\text{H}_2, \text{---} (7\text{C}_2\text{H}_2, \text{C}_6, \text{H}) = \text{C}_{24}\text{H}_{17}$ .

These radicals are known only in combination with oxygen as oxyhydrates. They possess weak acid properties, and combine with the strong bases to form salt-like compounds. By chlorine, bromine, and nitric acid, they are led over into the derived radicals of the salicyl group. The hydrates possess a highly sharp caustic taste; they coagulate albumen, and completely destroy the putrefying property of the protein combinations. They form by dry distillation many organic substances. Also, in urine, we have

recently discovered phenol and other compounds, which belong to the same groups.



*Phenol* (Spirol, Salicon) occurs in urine and in coal-tar, and is formed by dry distillation of salicylic acid and of salicin. Is most easily obtained when a mixture of hydrate of salicylic acid, with glass-powder or lime, is subjected to rapid distillation. Phenol goes over as colorless oil, which stiffens crystalline; it is colorless, crystallizes in long prismatic needles, melts at  $34^\circ$ , and boils at  $190^\circ$ ; sp. gr. = 1.061. The crystals become fluid, when exposed to the air, without absorbing water. Possesses extremely smoky smell and a burning caustic taste, dissolves with difficulty in water, but is soluble, in all proportions, in alcohol and ether; coagulates albumen, precipitates the glue-solution. If we dip a fir-shaving in a solution of phenol, and then into hydrochloric acid, it is colored, in drying, dark blue.

*Chlorine* converts phenol into compounds, which correspond to the formulæ  $\text{HO, C}_4\text{H}_2\text{-(C}_6\text{, C}_2\text{H)} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ ;  $\text{HO, C}_4\text{H}_2\text{-(C}_6\text{, C}_2\text{Cl)} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ , and  $\text{HO, C}_4\text{Cl}_2\text{-(C}_6\text{, C}_2\text{Cl)} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$ . Nitric acid decomposes phenol extremely easy; each drop which comes in contact with phenol causes violent hissing, without forming nitrous acid. According to the continuance of the action, we obtain nitrophenilic acid  $\text{HO, C}_4\text{H}_2\text{-(C}_6\text{, C}_2\text{H)} \left\{ \begin{smallmatrix} \text{O} \\ 2\text{NO}_4 \end{smallmatrix} \right.$ , and pikrin-nitric acid  $\text{HO, C}_4\text{H}_2\text{-(C}_6\text{, C}_2\text{NO}_4) \left\{ \begin{smallmatrix} \text{O} \\ 2\text{NO}_4 \end{smallmatrix} \right.$ . If we treat phenol with nitric acid and chlorate of potassa, as a final product, we obtain chloranil. It combines with concentrated sulphuric acid, forming *phenol-sulphuric acid*  $\text{HO(C}_{12}\text{H}_5\text{O, SO}_3)\text{-SO}_3$ . Brought in contact with *potassium*, whilst hydrogen gas is evolved, phenol forms a compound consisting of  $\text{KO, (C}_{12}\text{H}_5\text{)O}$ . This phenol-potassa is also obtained by the use of hydrate of potassa; it is white, crystalline, easily soluble in water, alcohol, and ether. The baryta compound appears in crystalline scales.

*Phenol-sulphuric Acid:*  $\text{HO(C}_{12}\text{H}_5\text{O, SO}_3)\text{-SO}_3$ . A mixture of phenol and hydrated sulphuric acid is after 24 hours diluted with water, the solution is made to boil, and saturated whilst hot with carbonate of baryta. From the filtered solution baryta salt is separated in small crystals. From the baryta salt we obtain the acid, which, after evaporating the solution in vacuum, remains as a syrup-like fluid.

*Creosote:*  $\text{HO, C}_4\text{H}_2\text{-(2C}_2\text{H}_2\text{, C}_6\text{, H)O=HO, (C}_{14}\text{H}_7\text{)O(?)}$ . Creosote is a product of dry distillation of non-nitrogenous, as of nitrogenous

bodies; it occurs in beach-wood tar, in crude wood-vinegar, etc. We subject wood-tar to distillation until 56 per cent. are gone over. The distillate consists of two layers, of which the lower contains creosote. The distillate containing creosote, divided from the upper layer, is mixed with carbonate of potassa, until effervescence no longer takes place. The separated oil is afterwards distilled. What goes over first is removed, and that only is taken up which sinks under the water. Now we treat the obtained distillate with a solution of caustic potassa, of 1.12 sp. gr., in which creosote is dissolved; remove the solution from the separated oils, heat it to boiling, and leave it to cool slowly in the air. From the brown alkaline solution, the creosote is precipitated by dilute sulphuric acid, afterwards washed out with water, dissolved in alkali and heated, then again precipitated by sulphuric acid; and this operation is repeated so long as the solution of caustic potash retains a brown color. The pure creosote is an oily, colorless, penetrating fluid; odor unpleasant, smoky; taste burning, extremely sharp. Destroys the epidermis; refracts light like sulpho-carbonic acid, and is fluid even at  $27^{\circ}$ ; boiling point  $203^{\circ}$ ; sp. gr. 1.03. Water dissolves 1.25 creosote; on the other hand, 100 parts of creosote absorb 10 parts of water. Alcohol, ether, and acetic ether mix in all proportions with creosote. Creosote is a solvent for sulphur, phosphorus, most of the organic acids, the organic bases, fatty oils, resins, etc. Towards albumen and the remaining protein compounds it behaves like phenol. *Nitric acid* acts very violently upon creosote, likewise *chlorine* and *bromine*. Creosote reduces many metal oxides. Brought in contact with potassium, under evolution of hydrogen, a compound is obtained  $\text{KO}, \text{C}_{14}\text{H}_7\text{O}$ . Dry *hydrate of potassa* is dissolved in creosote with evolution of heat, and forms a thick oily combination, which, by absorption of water, after a short time crystallizes in leaflets of mother-of-pearl lustre; the crystals deliquesce in the air.

Guaiacol.

*Guaiacol*:  $\text{HO}(\text{C}_{14}\text{H}_7)\text{O}_4(?)$ , is formed by the dry distillation of the guaiacum of commerce. The obtained oily product of distillation is washed with water, and then, as was shown with creosote, alternately treated with solution of potassa and sulphuric acid, until the alkaline solution is no longer colored in the air. Occurs as a clear colorless fluid, odor peculiar, taste piquant, peppery, boils at  $210^{\circ}$ , sp. gr. 1.119; volatile, slightly soluble in water, but easily so in alcohol and ether; the alkaline solution exposed to the air, after a short time grows dark colored, and forms with bases crystallizable salts.

*Carvacrol*:  $\text{HO}, \text{C}_4\text{H}_2(7\text{C}_2\text{H}_2, \text{C}_6, \text{H})\text{O} = \text{HO}, (\text{C}_{24}\text{H}_{17})\text{O}$ . Carvacrol is formed by the action of hydrate of potassa, iodine, and fused phosphoric acid upon cumin oil and thuja oil, as well as by the action of iodine upon camphor. We distil cumin oil with fused phosphoric acid in a flask with a long neck, until the smell of the



cumin oil has vanished, whilst we repeatedly pour back the distillate into the flask, where at length is found carvacrol, as an oil above the phosphoric acid. It is removed from the phosphoric acid and distilled in a retort; the first and last parts which go over are removed; a colorless, thick-flowing liquid, odor like creosote, taste extremely caustic, heavier than water, in which it is soluble, as also in alcohol and ether; coagulates albumen, and agrees mainly in its properties with creosote; boils at  $232^{\circ}$ . Towards potassium and potassa it behaves like the former compound.

*Picamar, kapnomar, cedriret, pittakal, rosolic acid, brunolic acid, and assamar* are products of dry distillation, which, in part, agree in their relations with creosote, but whose constitution is not yet known.

d. Pairling  $C_4H_2$ ; Component  $C_2H_2$ ; Nucleus  $C_6$ ; Active part  $C_2H$ .

Primary Radical:  $C_4H_2\text{---}(C_6, C_2H)=C_{12}H_3$ .

*Bichlorphenolic Acid* (Chlorphenessic Acid):  $HO$ ,  $C_4H_2\text{---}(C_6, C_2H) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$  is formed by the first action of Bichlor-phenolic acid.

chlorine upon phenol; oily, volatile, soluble in alcohol. It behaves to phenol as oxychloride of acetyl to alcohol. By action of nitric acid it is converted into *nitro-chlorphenolic* (nitro-chlorphenessic) *acid*,  $HO_4(C_{12}H_2, NO) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$ , which crystallizes in oblique rhombic yellow prisms; little soluble in water, but easily soluble in alcohol and ether.

*Terchlorphenolic Acid* (Chlorphenessic Acid):  $HO$ ,  $C_4H_2\text{---}(C_6, C_2Cl) \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$  is formed by the action of Terchlor-phenolic acid.

chlorine upon phenol, upon indigo, anilin, and chloranilin. Into tar-oil, which boils between  $170$  and  $190^{\circ}$  (and is rich in phenol), we conduct chlorine a long time, and then distil in a closed furnace. The first and last portions which go over are removed, and the obtained distillate brought in contact with chlorine, until the mass hardens and separates. The obtained mass is heated with water and ammonia to boiling, and the solution filtered. After cooling, the ammonia salt separates in crystals. These are dissolved in pure water, and decomposed with hydrochloric acid, whereby the terchlorphenolic acid is precipitated. It crystallizes from the solutions as well as by sublimation in long, white, very fine needles of silky lustre, melting at  $44^{\circ}$ , and stiffening in direct microscopic prisms. It possesses a penetrating odor, is not easily soluble in water, but easily in alcohol and ether; the solutions react acid; also soluble in fuming sulphuric acid. Boiling *nitric acid* converts the acid into a yellow substance crystallizing in spangles. The *ammonia salt* crystallizes in needles, likewise the *baryta salt*; the *lime salt* appears as a white, jelly-like precipitate.



*Pentachlor-phenolic Acid* (Chlorphenussic Acid):  $\text{HO}, \text{C}_4\text{Cl}_2 \wedge (\text{C}_6, \text{C}_2\text{Cl}) \left\{ \begin{array}{c} \text{O} \\ \text{Cl}_2 \end{array} \right.$ , is formed, if the former compound be exposed to the farther action of chlorine; it is farther produced by decomposition of chlorisatin by chlorine. Quite equals the former compounds, only it is less fusible, and its ammonia salt less soluble in water.

*Terbromphenolic Acid* (Bromphenisic Acid):  $\text{HO}, \text{Bromphenolic acid.} \left( \text{C}_4\text{H}_2 \wedge (\text{C}_6, \text{C}_2\text{Br}) \left\{ \begin{array}{c} \text{O} \\ \text{Br}_2 \end{array} \right. \right.$  Bromine is added to phenol

until an effervescence takes place, and finally it is gently warmed. After cooling, a brown mass remains, which is boiled with ammonia and water. From the solution of the ammonia salt, which crystallizes in needles, the acid is precipitated by hydrochloric acid. Crystallizes in very thin, colorless needles, and quite equals the corresponding chlorine compound, but is less soluble in alcohol and ether.

*Nitrophenolic Acid* (Nitrophenesic Acid):  $\text{HO}, \text{Nitrophenolic acid.} \left( \text{C}_4\text{H}_2 \wedge (\text{C}_6, \text{C}_2\text{H}) \left\{ \begin{array}{c} \text{O} \\ 2\text{NO}_4 \end{array} \right. \right.$ , is obtained by the action of

nitric acid upon phenol and upon coal-tar, whose boiling point is between  $160^\circ$  and  $190^\circ$ , and which is rich in phenol. Crystallizes in whitish-yellow prisms with rectangular bases, which, in thin layers, are almost colorless. Inodorous, at first tasteless, afterwards bitter, fuses at  $140^\circ$ , and stiffens to a fibrous leafy mass; only slightly soluble in boiling water, easily soluble in ether, and in 4 parts alcohol; colors the skin, hair, and, especially animal membrane, yellow. Detonates by sudden heating. The salts are yellow, crystallizable, and almost all soluble in water; their solutions color the skin deeply yellow; they detonate feebly in high temperatures, and in a closed vessel with evolution of light. They are obtained either direct or, like the lead salt, by double affinity.

*Pikrin-nitric Acid* (Nitrophenesic Acid, Indigo-bit-  
*Pikrin-nitric acid.* ter):  $\text{HO}, \text{C}_4\text{H}_2 \wedge (\text{C}_6, \text{C}_2, \text{NO}_4) \left\{ \begin{array}{c} \text{O} \\ 2\text{NO}_4 \end{array} \right.$ , is formed by

the action of nitric acid upon the former compound, and farther by the continued action of nitric acid upon indigo, besides nitro-salicylic acid upon aloes, silk, salicin, salicylous and salicylic acid, coumarin, phloridzin, populin, and upon other non-nitrogenous as well as nitrogenous compounds. Nitrophenolic acid is boiled a few minutes with nitric acid; we obtain pikrin-nitric acid, which is purified by solution in alcohol, and repeated crystallization.

*From Indigo:* In a spacious flask 18 to 20 parts nitric acid of 1.130 sp. gr. is brought nearly to boiling, and to this is added, little by little,  $1\frac{1}{2}$  parts coarsely broken indigo. The reddish-brown fluid is boiled, until it is somewhat thick; after cooling, yellow, semitransparent, hard crystals form, which are washed with water.

The crystals are dissolved in a large quantity of boiling water, the drops of oil which separate removed, and filtered. A large quantity of gold-colored, shining, leafy crystals separate, which are afterwards dissolved in boiling water. We neutralize the solution with carbonate of potassa, and purify the pikrino-nitrate of potassa by repeated crystallization. The pure potassa salt is dissolved in boiling alcohol, and the solution decomposed by hydrochloric acid. After cooling, the pikrino-nitric acid precipitates in yellow, remarkably shining leaflets.

*From Aloes:* One part aloes with 8 parts strong nitric acid is gently warmed; when the first action is over, the yet present nitric acid is distilled off in a retort; to the residue is added gradually 3 to 4 parts nitric acid, and the whole heated for a few days to boiling. The residue is mixed with much water, whereby a mass of a greenish-yellow color is precipitated, which is impure *chrysamminic acid*, whilst in the solution is found pikrin-nitric acid with oxalic acid.

The acid crystallizes in equilateral prisms, whose primary form is a rhombic octohedron. It is in a very scanty portion soluble in cold water; in boiling water it is more easily dissolved. The solution has a dark brown color, and an intensive bitter taste; it is easily dissolved in ether, alcohol, nitric acid, and other mineral acids. Slowly heated in the air, it first melts to a brown yellow liquid, and by stronger heating sublimes under diffusion of a thick yellow, suffocating odor, which when inspired produces an intolerable suffocation. Quickly heated, it burns with a clear light flame. Gently warmed in a retort with peroxide of *manganese* and *sulphuric acid*, it evolves nitrous acid. If an intimate mixture of *pikrin-nitric acid*, *sulphate of protoxide of iron*, be digested with water and *hydrate of baryta*, thus by reduction is obtained *rubrin-nitric acid* (hematin-nitric acid); it crystallizes in small, brown, almost tasteless granules, dissolves with difficulty in water, with a yellow color, and when drenched in an alkaline solution dissolves with a beautiful intense blood-red color. A mixture of *hydrochloric acid* and *chlorate of potassa* converts pikrin-nitric acid into chloranil. If it be boiled with potassa, it evolves pure ammonia. The salts are crystallizable, possess a bitter taste, and explode violently if they are quickly heated. The *ammonia salt* crystallizes in beautiful yellow, six-sided columns; by heating loses ammonia under sublimation of the acid. The potassa salt appears in direct prisms with rhombic bases, and possesses a beautiful deep red color. It requires 260 parts water of 16° for solution; it is dissolved in larger quantity by boiling water; insoluble in alcohol. Pikrin-nitric acid combines with *oxide of lead* in several proportions, forming *penta-*, *ter-*,  $\frac{2}{3}$ -, *semi-*, *sesqui-*, and *uniacid salts*. The last gives a double salt with acetate of lead.

**Chlorpikrin.** *Chlorpikrin.* If an aqueous solution of pikrin-nitric acid be distilled with chloride of lime, colorless heavy oil passes over with the aqueous vapor. This oil strongly refracts light, and in dilute condition possesses a peculiar aromatic odor; when concentrated it violently excites the nose and eyes; insoluble in water, easily dissolves in alcohol and ether; sp. gr. 1.665; boils at 120°. Is not attacked by nitric, sulphuric, or hydrochloric acid, but on the other hand is decomposed by an alcoholic solution of potassa, with formation of chloride of potassium and nitrate of potassa. This body is said to consist of  $C_4Cl_7N_2O_{10}$ . Is also obtained by the action of chloride of lime upon chrysaminic and oxypikrin-nitric acid.

**Oxypikrin-nitric acid.** *Oxypikrin-nitric Acid:*  $2OH, C_4H_2(C_6, C_2, NO_4)$   
 $\left\{ \begin{array}{l} O_3 \\ 2NO_4 \end{array} \right. (?)$ . This acid, which contains two atoms more

oxygen than pikrin-nitric acid, is formed by the action of nitric acid upon euxanthin and euxanthon, as well as by the action of the same upon ammonia-gum, assafetida, galbanum, sagapenum, upon the watery extract of Brazil wood, sandal wood, and fustic; at the same time the formation of oxalic acid does not take place. (Fluid storax, dragon's blood, and opoponax give no oxypikrin-nitric acid.) We obtain this acid in a similar way by the use of assafetida, as pikrin-nitric acid from indigo or aloes. From the extract of Brazil wood it is obtained by warming the extract to 40° with from 4 to 6 times its weight of concentrated nitric acid of 1.37 sp. gr. As the first furious action is over, and the extract changed into a dark red-brown fluid, the bowl is again placed over the fire, and the oxidation continued, until by farther evaporation, upon the addition of water, the oxypikrin-nitric acid is precipitated as a yellow white, sandy powder. From the alcoholic solution the oxypikrin-nitric acid gives well-formed, tolerably thick crystals of 3 to 4 lines long. It is dissolved in 88 parts water at 62°; easily soluble in alcohol and ether; dissolves rather easily in acids. The solution colors the skin permanently yellow. It possesses an astringent, either bitter or sour taste. The acid melts by cautious heating upon platinum foil, and stiffens to a radiated, crystalline mass; volatilizes by boiling in water. Quickly heated, the acid feebly detonates. *Nitric and hydrochloric acids* do not act upon it. Treated with the *sulphate of protoxide of iron* and baryta water, it forms a colorless baryta salt. If the alcoholic solution be warmed with *sulphide of ammonium*, and the dark brown fluid evaporated to dryness, there remains a black mass which consists of sulphur, a black substance, and oxypikrin-nitrate of ammonia (?) A concentrated solution of potassa decomposes the acid by boiling. This acid differs from the pikrin-nitric acid essentially by its tendency to saturate two atoms base, one atom of which may be substituted by an atom of another base, whereby a numerous class of



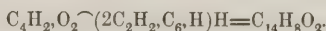
double salts arises. Almost all salts possess in a high degree the property, when gently heated, of exploding with extreme violence. The aqueous solution of the acid reacts sour, and it easily expels carbonic acid from its salts. Almost all the salts dissolve in water.

*Pikranisic Acid:*  $\text{HO}, \text{C}_{12}\text{H}_2\text{N}_3\text{O}_{13}$ . This acid, *Pikranisic acid*, isomeric with pikrin-nitric acid, is obtained if the so-named trinitranisol is boiled with moderately concentrated solution of potassa. A salt is obtained scarcely soluble in water, which crystallizes from the boiling solution in long, brownish-yellow needles. Boiling dilute nitric acid separates, thence the pikranisic acid, which crystallizes from the hot saturated aqueous solution in yellow shining needles. It is easily soluble in boiling water, alcohol, and ether. The acid dissolves oxide of silver, and by slow evaporation we obtain the silver salt in fine, orange-yellow needles. The *soda salt* crystallizes in long, gold-colored needles.

e. Pairing  $\text{C}_4\text{H}_2\text{O}_2$ ; Component  $\text{C}_2\text{H}_2$ ; Nucleus  $\text{C}_6$ ; Active element H.

#### SECOND MEMBER.

#### ANISE OIL:



*Anise Oil* (Anisol) is obtained when the hydrate of anisic acid, mixed with an excess of baryta, is submitted to distillation; or we let the spiroylate of methyl fall in drops upon heated baryta. The obtained anise oil is washed with a solution of potassa and water, and distilled over chloride of calcium. A colorless, very mobile fluid, of agreeable, aromatic odor, insoluble in water, easily soluble in alcohol and ether; boils at  $152^\circ$ , sp. gr. 0.991. Gives with bromine *brom-anise oil*, with nitric acid *nitro-anise oil*, and with sulphuric acid *sulph-anise oil*.

*Brom-anise Oil* (Bromanisol):  $\text{C}_4\text{H}_2\text{O}_2 \wedge (2\text{C}_2\text{H}_2, \text{C}_6, \text{H})\text{Br}$ , *Brom-anise oil*, arises by the action of bromine upon anise oil; not known in pure state.

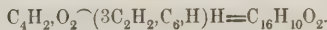
*Nitro-anise Oil* (Nitroanisol):  $\text{C}_4\text{H}_2\text{O}_2 \wedge (2\text{C}_2\text{H}_2, \text{C}_6, \text{H})\text{NO}_4$ , *Nitro-anise oil*. We add to anise oil, cooled by ice, fuming nitric acid in small portions. A blue-black fluid, of an oily consistence, is obtained, which is washed with a solution of potassa and water, and then distilled. At  $160^\circ$  the pure compound passes over. Clear, amber-yellow fluid, insoluble in water, of agreeable odor, resembling oil of bitter almonds; boils at  $162^\circ$ ; is not decomposed by a solution of potassa. If we mix the alcoholic solution with sulphide of ammonium, we obtain, with separation of sulphur, an organic base, anisidin. By continued action of nitric acid, *nitro-anise oil* is converted into *salicyl-nitrid*  $\text{C}_4\text{H}_2\text{O}_2 \wedge (\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})3\text{NO}_4$ .



Sulph-anise oil. *Sulphanise Oil* (Sulphanisol):  $C_4H_2, O_2 \wedge (2C_2H_2, C_6, H) \wedge SO_2$ . We lead into cooled anise oil the vapor of anhydrous sulphuric acid, mix the thick mass formed with water, whereby the sulphanise oil is precipitated in fine needles; it is washed with water, and crystallizes from alcohol; appears in tender needles of silver lustre, insoluble in water, sublimable, and combines with concentrated sulphuric acid, forming *sulphanise-oil-sulphuric acid*  $HO, C_4H_2, O_2 \wedge (C_2H_2, C_6, C_2H) \wedge SO_2, \wedge SO_3$ . Is also obtained if anise oil be dissolved in the same weight of hydrate of sulphuric acid, the solution diluted with water, and then saturated with carbonate of baryta. From the filtered solution we obtain by evaporation crystals of sulphanise-oil-sulphate of baryta.

## THIRD MEMBER.

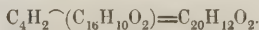
## PHENETOL:



We obtain phenetol when a mixture of baryta and salicylate of ethyl is submitted to dry distillation. A colorless fluid, boils at  $172$  to  $175^\circ$ , insoluble in water, easily soluble in alcohol and ether. Gives with bromine bromphenetol  $C_4H_2, O_2 \wedge (3C_2H_2, C_6, H)Br$ ; with *nitric acid* nitrophenetol  $= C_4H_2, O_2 \wedge (3C_2H_2, C_6, H)NO_4$ , and with concentrated *sulphuric acid* sulphophenetol-sulphuric acid.

## PAIRED COMBINATIONS OF PHENETOL.

## ANISE CAMPHOR:



*Anise-camphor* is the solid part of anise oil, which is procured from the seed of *Pimpinella anisum* by distillation with water. This substance is also found in fennel oil, and stellated anise oil. Crude, coagulated anise oil is pressed between blotting paper until the latter no longer becomes spotted, and the solid part repeatedly crystallized from alcohol. It appears in white, remarkably shining leaflets, of pleasant, anise-like odor; sp. gr. 1.014, boils at  $220^\circ$ , is pulverizable at  $0^\circ$ , and melts at  $18$  to  $20^\circ$ .

*Dilute nitric acid* converts anise-camphor into anisylous and anisylic acid; treated with *concentrated acid*, we obtain nitro-anisid  $= C_{20}H_{10}O_2, 2NO_4$ . *Chlorine* and *bromine* change it into  $2C_4H_2 + O_2 \wedge (2C_2H_2, C_6, C_2H)Cl_3$ , &  $2C_4H_2 + O_2 \wedge (2C_2H_2, C_6, C_2H)Br_3$ .

If 1 part anise-camphor be mixed with  $1\frac{1}{2}$  parts sulphuric acid, we obtain a resinous mass, from which arises, by treatment with water, *anisoin*,  $C_{40}H_{24}O_4$ . Heated with hydrate of potassa, we obtain an acid not yet investigated.

*Nitroanisid*:  $C_{20}H_{10}O_2, 2NO_4$ , a body insoluble in the different

solvents; melts at  $100^{\circ}$ , non-volatile. Decomposes, by boiling with potassa solution, under production of a black, acid substance.

*Chloranise Oil* (Chloranisol):  $C_{20}H_9O_2Cl_3$ , is colorless, at ordinary temperature, syrup-thick, not volatile.

*Bromanise Oil* (Bromanisol):  $C_{20}H_9O_2Br_3$ , forms, from the etheric solution, shining voluminous crystals, grates between the teeth; insoluble in water, not easily soluble in alcohol, more easily soluble in ether; decomposes even at  $100^{\circ}$ .

*Dracunculus Oil* (Esdragonol):  $C_{20}H_{12}O_2$ . This compound, isomeric with anise-camphor, is found in the leaves of *Artimesia dracunculus*. Colorless, fluid oil, smelling like dracunculus: boils at  $206^{\circ}$ ; dissolves in an equal quantity of pure water, and in all proportions in ether. By the action of nitric acid, it is converted into anisylic and nitro-anisylic acid.

*Anisoïn*:  $C_{40}H_{24}O_4$ . Metameric with anise-camphor. Arises by the action of sulphuric acid upon Anisoin. anise-camphor. Almost completely white, inodorous, melts at  $200^{\circ}$ , heavier than water, in which it is insoluble; not easily soluble in alcohol, more easily soluble in ether, and separates from the etheric solution in small crystalline needles; partly volatile.

f. Pairling  $C_4H_2O_2$ ; Component  $C_2H_2$ ; Nucleus  $C_6$ ; Active part  $C_2H$ .

#### FIRST MEMBER.

#### SALICYL:

SPIROYL: Sa.  $C_4H_2O_2 \sim (C_2H_2, C_6, C_2H) = C_{14}H_5O_2$ .

*Salicyl* is found, as salicylous acid, in the flowers of *Spirea ulmaria*, and as salicylic acid combined with oxide of ethyl in the oil of the *Gaultheria procumbens* (winter-green). Arises by oxidation of saligenin, by heating indigo, salicin, coumarin, etc., with hydrate of potassa.

*Hydrate of Salicylous Acid* (Hydrate of Spiroylous Acid, Hydrosalicylous Acid):  $HO, C_4H_2O_2 \sim (C_2H_2, C_6, C_2H)O = HO, SaO$ , is found in the flowers of *Spiræa ulmaria*, and is formed from oxidation of saligenin by chromic acid. The dry flowers of the *Spiræa ulmaria* are distilled with water, until what comes over is no longer colored yellow by potassa. The obtained distillate is accurately saturated with potassa, and the solution evaporated to dryness under exclusion of air. The residue is distilled with a corresponding quantity of phosphoric acid; a part of the acid separates, like oil from the distillate, another part remains dissolved in the water; or, we distil a mixture of 3 parts salacin, 3 parts acid chromate of potassa,  $4\frac{1}{2}$  parts sulphuric acid, and 36 parts water; when the evolution of gas has ceased, the distillation is continued, until drops of oil go over. We dry the acid by chloride of calcium, and rectify it. In a pure state it is an almost colorless oil of the remarkable odor of the blossom of *spiræa*; tastes sharp

and burning, and leaves a white spot upon the tongue; not easily soluble in water. The solution reddens litmus tincture in the beginning, and, little by little, completely bleaches it; miscible in all proportions with alcohol and ether; at  $20^{\circ}$  becomes solid; boils at  $195^{\circ}$ ; sp. gr. = 1.1731. In the air salicylous acid suffers no essential change; but if an *alkaline solution* of that substance be brought in contact with *oxygen*, the solution is colored black under production of *acetic* and *melanic acid*,  $C_4H_2O_2 \cdot (C_2H_2, C_6, C_2H)O + 2HO + 3O = C_4H_3O_3 + C_{10}H_4O_5$ . If the acid be heated with an excess of hydrate of potassa, *salicylic acid*,  $C_4H_2O_2 \cdot (C_2H_2, C_6, C_2H)O_3$ , is obtained under evolution of hydrogen gas. *Chlorine*, *bromine*, and *nitric acid*, convert it into derived compounds.

*Salicylous Acid Salts.* Salicylous acid expels carbonic acid from its combinations; it forms neutral and acid Salicylous acid salts, some of which are soluble, with difficulty, in water, and some insoluble. Very dilute solutions of the acid are immediately colored yellow by potassa; *salts of peroxide of iron* produce an intense violet color in a solution of the acid, and of the salt.

*Salicylite of Ammonia.* If the acid be brought to concentrated ammonia, the whole sets to a yellow crystalline mass, insoluble in water. If ammonia gas acts upon the acid, we obtain yellow crystals. They easily decompose into ammonia and acid.

*Salicylimid-amid* (Spiroylimid):  $NH_2Sa + NH_2, 2Sa$ . If an alcoholic solution of salicylous acid be brought together with aqueous ammonia, yellowish-white little spears are formed, which dissolve by warming; after cooling, heavy, deep-yellow crystals of salicylimid-amid separate. Insoluble in water, not easily soluble in alcohol, unchanged in the air; melt at  $300^{\circ}$  to a brown-yellow mass under sublimation of a light white substance. *Weak acids* do not act upon the compound in the cold, but, by heating, an ammonia salt and salicylous acid arise; *caustic potassa* produces, by boiling, the same decomposition. If to a dilute alcoholic solution of salicylimid-amid, oxide of copper and ammonia be added, thus is produced, after 10 to 12 minutes, remarkably shining, light crystal leaflets of salicylimid-copper. This compound consists of  $Cu_3N$  + salicylimid-amid. After drying, the crystals appear very light, fiery, dark-green, and satin-lustred; insoluble in water and alcohol.

*Salicylimid-iron*:  $Fe_2N$  + salicylimid-amid, is obtained, when a solution of perchloride of iron, decomposed with tartaric acid, is brought together with a hot prepared alcoholic solution of salicylimid-amid mixed with ammonia. It forms a yellow-red precipitate, which, after drying, appears dark fiery-red. Also a *lead compound* is known.

*Simple Salicylite of Potassa*:  $KO, SaO + 2aq.$ , appears in yellow quadratic tables of mother-of-pearl lustre; is obtained, when to an



alcoholic solution of salicylous acid potassa is added, until the mass is solid.

The *Acid Salt*:  $\text{KO}, \text{HO}, 2\text{SaO}$ , crystallizes in fine, yellowish white, tuftifor-grouped needles, like quinin. The *baryta compound* appears as a beautiful, yellow, crystalline powder. The *basic lead compound*,  $2\text{PbO} + \text{SaO}$ , is precipitated, if a solution of salicylous acid is mixed with basic acetate of lead.

The *Copper Salt*,  $\text{CuO}, \text{SaO}$ , is deposited in brownish-green crystals, if, in the cold, a solution of neutral acetate of copper be added to a dilute alcoholic solution of salicylous acid; decomposes, by dry distillation, into salicylous acid, parasalicyl, and salicylate of protoxide of copper, with a few other products.

*Bichlorsalicylous Acid*:  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \wedge (\text{C}_2\text{Cl}_2, \text{C}_6, \text{C}_2)$  Derived radicals of salicyl.  $\text{H})\text{O}$ , is known only in combination with salicylous acid. This double acid  $2\text{HO}(\text{C}_{14}\text{H}_3\text{O}_2\text{Cl}_2)\text{O}^- + \text{SaO}$ , is obtained if chlorine be conducted slowly over hydrate of salicylous acid until no more evolution of hydrochloric acid gas is observed. The salicylous acid changes into a white, crystalline mass, which crystallizes from the alcoholic solution in right-angled plates of mother-of-pearl-lustre; it possesses a bitter, aromatic odor, resembling bitter almond oil; insoluble in water, easily soluble in alcohol and ether. Gives with bases salts, mostly yellow, and soluble with difficulty, or insoluble in water. If anhydrous ammonia be conducted over the acid, we obtain a combination of *salicylimidamid* with *bichlorsalicylimidamid*, which crystallizes from the hot alcoholic solution in small, yellow, tasteless scales, insoluble in water.

*Bibromsalicylous Acid*:  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \wedge (\text{C}_2\text{Br}_2, \text{C}_6, \text{C}_2)$  Bibromsalicyl.  $\text{H})\text{O}$ , is obtained if bromine be added to an alcoholic solution of salicylous acid, until the color no longer vanishes; the whole becomes warm, and after cooling yellow lanciform crystals separate, which are purified by recrystallization. Crystallizes in rather large, firm, quadratic columns, of pale yellow color; it melts easily upon the water bath, sublimes, and possesses an agreeable, benzoic odor; quite insoluble in water, easily soluble in alcohol and ether. The alcoholic solution colors litmus and indigo. If hydrosulphuric acid be led into the warm alcoholic solution of the acid mixed with ammonia, a brown resinous body is precipitated, which consists of  $\text{C}_{14}\text{H}_6\text{O}_2\text{S}_2\text{Br}_2$ . With bases it forms salts, mostly yellow.

*Bibromsalicylous Acid* combines with salicylous acid, forming a double acid  $= 2\text{HO}(\text{C}_{14}\text{H}_3\text{O}_2\text{Br}_2)\text{O}^- + (\text{C}_{14}\text{H}_5\text{O}_2)\text{O} = \text{HO}, (\text{C}_{14}\text{H}_4\text{O}_2\text{Br})\text{O}$ . We obtain the compound if bromine be very slowly conducted over salicylous acid, or if we mix a solution of bibromsalicylous acid with salicylous acid, and precipitate with water. A resinous precipitate forms, which immediately becomes solid. It is dissolved in alcohol, and left to spontaneous evaporation. Crys-



tallizes in small, white, ciliary, quadratic columns, which have a wool-like appearance; insoluble in water, easily soluble in alcohol; bleaches coloring matter. If *hydrosulphuric acid* be led into the boiling solution, mixed with ammonia, there separates by mixing with water a resinous body, which consists of  $\text{HO}(\text{C}_{14}\text{H}_4\text{Br})\left\{\begin{smallmatrix} \text{O} \\ \text{SO}_2 \end{smallmatrix}\right. + \text{HO}(\text{C}_{14}\text{H}_5)\left\{\begin{smallmatrix} \text{O} \\ \text{SO}_2 \end{smallmatrix}\right. (?)$ . Gives with ammonia a combination consisting of *bibromsalicylimidamid* and *salicylimidamid*. The salts have a yellow color.

*Chrysanisic acid.*  $\text{C}_{14}\text{H}_4\text{O}_2, 3\text{NO}_4 = \text{HO}, \text{C}_4\text{H}_2\text{O}^-(\text{C}_2, 2\text{NO}_4, \text{C}_6, \text{C}_2\text{H})\text{NO}_4(?)$  We boil nitroanisic acid with threefold its weight of fuming nitric acid half an hour, and pour the fluid into 20 times its volume of water. There falls a mixture of bi- and trinitranisol with chrysaminic acid, which last is absorbed by ammonia from the mixture. From the ammonia salt purified by recrystallization the acid is separated by nitric acid. From the alcoholic solution it crystallizes in small, shining, gold-yellow, rhombic leaflets; scarcely soluble in water, alcohol, and ether; fuses by gentle warming, and sublimes. Boiled with concentrated nitric acid it changes into pikrino-nitric acid. Gives with *potassa* an easily soluble salt. The *ammonia salt* crystallizes in small brown needles; the *ethyloxyd compound* in shining, gold-yellow leaflets.

*Nitro-salicylous Acid:*  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2^-(\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2, \text{NO}_4)\text{O}$ . If salicylous acid be gently warmed with dilute nitric acid, we obtain, without production of nitrous acid, a solid crystalline mass, which crystallizes from the alcoholic solution in transparent, yellow prisms. Almost inodorous, does not taste remarkable at first, but produces afterwards a violent itching in the œsophagus; fuses easily, and stiffens crystalline; soluble, with difficulty in water, but easily in alcohol, and ether; colors the skin and nails permanently yellow; sublimable. We obtain the *salts of the alkalies* in yellow crystals. The *lead compound* appears as a yellow powder, the copper as a green one. By boiling with fuming nitric acid, the acid is converted into pikrinnitric acid. Nitro-salicylous acid is double, consisting of salicylous acid, and binitro-salicylous acid.

*Salicylic (Spiroylic) Acid:*  $\text{C}_4\text{H}_2, \text{O}_2^-(\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3 = \text{C}_{14}\text{H}_5\text{O}_5$   
*Salicylic acid.*  $= \text{SaO}_3$ .

*Salicylic Acid* is formed by the oxidation of salicylous acid. It occurs in nature, in combination with oxide of methyl, in oil of *Gaultheria procumbens*; it is, farther, obtained if saligenin, salicin, coumarin, or indigo is heated with hydrate of potassa, as well as by dry distillation of salicylite and benzoate of copper.

*Hydrate of Salicylic Acid:*  $\text{HO}, \text{SaO}_3$ . The oil of the *Gaultheria procumbens* is exposed, with a concentrated solution of potassa, to the temperature of  $45^\circ$ ; wood-spirit, which volatilizes, and a solution of salicylate of potassa, are formed; from the latter, salicylic

acid is precipitated by hydrochloric, or sulphuric acid; or, we heat hydrate of salicylous acid, or salicin, with an excess of hydrate of potassa; when no more hydrogen is evolved, the mass is removed from the fire, dissolved in water, and the salicylic acid precipitated by sulphuric acid. It separates from the hot aqueous solution in long friable crystals; from the alcoholic solution we obtain the acid in voluminous, brittle, four-sided prisms; by very slowly evaporating the etheric solution in a high cylindrical glass, we obtain crystals 3 to 4 centim. long, and 4 to 6 milim. broad. Slightly soluble in cold water, abundantly in hot, and easily soluble in alcohol and ether; possesses a sweetish taste, irritating the œsophagus; the solutions redden litmus; melts at  $150^{\circ}$ ; completely sublimes. If suddenly exposed to a high temperature, it decomposes into phenol and carbonic acid. Gives, with fuming *nitric acid*, derived products; likewise by the action of chlorine and bromine. Warmed with *hydrochloric acid* and *chlorate of potassa*, chloranil arises. With anhydrous sulphuric acid, it gives a paired sulphur acid, which forms, with most bases, soluble salts.

*Salicylic Acid Salts.* The compounds with ammonia, potassa, soda, baryta, strontia, lime, magnesia, and oxide of zinc, are easily soluble in water, and those with oxide of lead, copper, and silver, soluble with difficulty. If a drop of *nitrate of peroxide of iron* be brought upon a crystal of salicylic acid, it is colored black as ink; if the acid be dissolved in water, a trace of the iron salt is sufficient to diffuse a violet color through the fluid. Salicylic acid expels carbonic acid from its compounds; from the concentrated solution of the salt, the latter is mostly precipitated by hydrochloric acid; it forms only neutral salts. The *ammonia salt* crystallizes in white needles of a silky lustre. If the salt be submitted to dry distillation, it decomposes into water, and *salicylamidic acid*  $= \text{NH}_2$ ,  $\text{C}_4\text{H}_2\text{O}_2(\text{C}_2\text{H}_2\text{C}_6\text{H}_5\text{O}_2)_2$ ; it is soluble, with difficulty <sup>Salicylamidic acid.</sup> in cold water, and easily in hot; crystallizes in quadrilateral prisms; fuses at  $100^{\circ}$ , and sublimes unchanged. Acids decompose the compounds into salicylic acid and ammonia.\* The

\* If indigo be boiled with a concentrated potassa solution, and to the concentrated solution, before the indigo-blue completely vanishes, if per-<sup>Anthranilic acid.</sup> oxide of manganese be added, in small portions, until a proof, dissolved in water, deposits no more indigo, the mass contains anthranilate of potassa. Now the crystallized anthranilic acid consists of  $\text{NC}_{14}\text{H}_7\text{O}_4$ , and, also, salicylamidic acid has the same constitution. Both compounds, however, are not identical. When the above-mentioned mass is dissolved in alcohol, and the excess of potassa is precipitated by carbonic acid, anthranilic acid is obtained; from the abfiltered solution, we obtain, by evaporation, anthranilate of potassa, in very small, thin leaflets, grouped together. If this salt be dissolved in a little water, we obtain, upon addition of acetic acid, *hydrate of anthranilic acid*,  $\text{HO}, \text{NC}_{14}\text{H}_6\text{O}_3$ . It crystallizes in yellowish, transparent leaflets of great lustre, and half an inch in length; in cold water not easily soluble, but easily in boiling; it is also taken up, in large quantities, by alcohol and ether; it melts at  $135^{\circ}$ , and sublimes similarly to benzoic acid. If it be heated to boiling, it separates into anilin,  $\text{NC}_{12}\text{H}_7$ , and carbonic acid; with the alkalis, it gives salts soluble in water and alcohol.

*potassa salt* is separated, by the evaporation of the aqueous solution in vacuum, in colorless, silky, lustrous crystals. The *oxide of lead salt* appears in beautiful, transparent crystals, and the *silver salt* in small, transparent, very lustrous crystals.

*Tribromanisol* (Spiroylbromid):  $C_4H_2O_2 \cdot (C_2H_2, C_6, C_2H)Br_3$ , is only known in combination with bromanisol, and produces the so-called bibromanisol:  $C_{14}H_7O_2Br + C_{14}H_5O_2Br_3 = C_{14}H_6O_2Br_2$ . We add bromine to anisol, mix the obtained product with water, and crystallize it from the boiling alcoholic solution. It appears in very shining scales; fuses at  $54^\circ$ ; sublimable.

*Salicylnitrid* (Trinitranisol):  $C_4H_2O_2 \cdot (C_2H_2, C_6, C_2H) 3NO_4$ . We treat anisol, or nitro-anisol, with a mixture of equal parts fuming sulphuric and fuming nitric acid, or, we warm gently 1 part anissic acid with 15 parts of the same mixture, and add water to the cooled mixture, thus the salicyl-nitrid is precipitated as a heavy oil, which quickly stiffens to a solid, light, yellow mass. It dissolves easily in a mixture of alcohol and ether, and separates by spontaneous evaporation in yellow, shining plates. Insoluble in water, melts at  $58$  to  $60^\circ$ , and if cautiously heated, may be sublimed. Warmed with concentrated potassa-lye, it is decomposed under formation of pikranisic acid. If the alcoholic solution be brought in contact with sulphide of ammonium, we obtain a base of binitro-anisidin, which consists of  $(C_{14}H_5O_2, 2NO_4) \cdot NH_2$ .

Binitranisol.

The so-called *Binitranisol*  $= C_4H_2O_2 \cdot (2C_2H_2, C_6, H)NO_4 + C_4H_2O_2 \cdot (C_2H_2, C_6, C_2H) 3NO_4 = C_{14}H_6O_2 + 2NO_4$ , is a compound of *salicyl nitrid* with *nitro-anisol*. It arises when anisol is boiled a few minutes with fuming nitric acid. Upon addition of water, a yellow liquid is separated, which soon hardens to an amber-yellow mass. From the boiling solution, the compound is separated in long, yellowish needles; insoluble in water, easily soluble in boiling alcohol and ether; fuses at  $86^\circ$ , sublim-

If to boiling concentrated potassa-lye of 1.45 sp. gr., which boils at  $150^\circ$ , we gradually add pulverized indigo-blue, after a little a deposition of small yellow crystals takes place, and, in cooling, the whole stiffens to a crystalline mass, whilst sometimes a yellow potassa salt, sometimes hydrate of potassa, is separated. This mass dissolves in water with brownish-yellow color; and, at the same time, indigo-blue is deposited. If the alkaline fluid be at once nearly saturated with an acid, a bluish green precipitate is formed, and in the fluid abfiltered from this precipitate, we obtain, by an excess of acid, an abundant flaky precipitate of *chrysanic acid*, which, after drying, contracts to a pulverizable reddish brown mass. If a mixture of equal parts alcohol and water be saturated at boiling heat with chrysanic acid, the greater part of the acid separates from the filtered solution in thick stelliform groups of very fine needles. The acid is said to consist of  $HO, N_2C_{28}H_{10}O_5$ , but it is probably a mixed substance. If it be boiled with a dilute mineral acid, it decomposes completely into anthranilic acid, which remains dissolved, and another body, which is deposited in cooling, in very fine needles of deep, blue-black color; these two substances do not appear to have the same constitution. Chrysanic acid is easily dissolved in pure alkalis. When no excess of alkali is present, the solution has a golden-yellow color; but if an excess be present, the solution is colored greenish, and is covered, when exposed to the air, by a deep, blue layer.



able unchanged. By a potassa solution, it is converted into nitrophenesic acid. With sulphide ammonium it gives, in the alcoholic solution, a double base, consisting of anisidin and binitro-anisidin.

*Bichlorsalicylic Acid:*  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \cdot (\text{C}_2\text{Cl}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3$ . Into a moderately concentrated solution of salicylate of potassa, chlorine gas is slowly led as long as the brown precipitate, which is at once formed, is increased. This is impure bichlor-salicylate of potassa, which, by repeated crystallization from the hot, saturated, aqueous solution, is purified. From the pure potassa salt the acid is precipitated by hydrochloric acid. It is separated from the concentrated alcoholic solution in hard, easily-pulverized octahedrons; almost insoluble in water, very easily dissolved in alcohol and ether. *Nitric acid* decomposes the compound, forming nitro-chlorsalicylic acid. The *potassa salt* forms small, grayish-white crystals, soluble in boiling water. A compound of *bichlor-salicylic acid* with *salicylic acid* is obtained by the action of chlorine upon an excess of salicylic acid. Derived compounds of salicylic acid.

*Bibromsalicylic Acid:*  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \cdot (\text{C}_2\text{Br}_2, \text{C}_6, \text{C}_2\text{H})\text{O}_3$ . We treat finely pulverized salicylic acid with an excess of bromine. The decomposed mass is washed out with water, and then dissolved, boiling hot, in ammonia. From the solution of ammonia salt, the acid is precipitated by hydrochloric acid, and is purified by repeated crystallization out of alcohol. Crystallizes in colorless or pale-yellow needles; scarcely soluble in water, but easily soluble in alcohol and ether. The *potassa salt* is obtained, when bromine is added to a solution of salicylate of potassa; in water not easily soluble. If we let bromine act upon an excess of salicylic acid, we thus obtain a combination of *bibrom-salicylic acid* with *salicylic acid*, which double acid crystallizes from the boiling alcoholic solution, in colorless, very lustrous prisms. The salts are less soluble than the corresponding ones of salicylic acid.

*Tribrom-salicylic Acid:*  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \cdot (\text{C}_2\text{Br}_2, \text{C}_6, \text{C}_2\text{Br})\text{O}_3$ , is obtained, when bibrom-salicylic acid is exposed with bromine to the sunlight for 20 to 30 days. From the alcoholic solution it crystallizes in small, yellowish, easily pulverized prisms; insoluble in water, rather easily soluble in alcohol. With soda, potassa, and ammonia, it gives salts scarcely soluble in water.

*Binitro-salicylic Acid:*  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2 \cdot (\text{C}_2\text{NO}_4, \text{C}_6, \text{C}_2\text{H})\text{O}_3$ . If binitro-salicylate of methyl, which is obtained by the action of a mixture of equal parts fuming sulphuric acid and fuming nitric acid, be boiled with dilute potassa lye, we obtain binitro-salicylate of potassa as a beautiful red salt, out of which the acid is precipitated by sulphuric acid. It crystallizes from the hot aqueous solution in needles of silky lustre; is easily dissolved in ether, alcohol, and hot water; fusible, and by being cautiously heated sublimable. The *ammonia salt* appears in small yellow needles;



it gives with *potassa* a *neutral* and a *basic* compound; the latter contains two atoms *potassa*, the former exhibits a crystalline, chrome-yellow powder, soluble in a large quantity of water; the latter compound possesses a beautiful red color.

If we dissolve salicylic acid in moderately concentrated nitric acid, and digest the solution a short time upon the water bath, in cooling a combination of *binitro-salicylic acid* with *salicylic acid*  $=\text{HO},\text{C}_{14}\text{H}_4,\text{NO}_4\text{O}_5$  is separated, which is called *nitro-salicylic acid*. The same compound is also obtained by the action of nitric acid upon indigo (indigotic acid) and salicylate of methyl. Crystallizes in white, stellated needles, possesses a bitter, astringent, feebly acid taste, sublims by being cautiously heated; requires 1000 parts cold water for solution, but dissolves in boiling water in every proportion; in a crystalline condition it contains 4 atoms water; it expels carbonic acid from its combinations. Its salts are mostly yellow; a solution of the acid colors the *salts of the peroxide of iron* red. If nitro-salicylate of methyl be treated with ammonia, after evaporating the solution, nitro-salicylamidic acid is obtained in small shining needles; they consist of  $\text{NH}_2,\text{SaO}_2+\text{NH}_2,\text{C}_4\text{H}_2\text{O}_2\text{-(C}_2\text{NO}_4,\text{C}_6,\text{C}_2\text{H)}\text{O}_3$ .

*Trinitro-salicylic Acid*:  $\text{HO},\text{C}_4\text{H}_2\text{O}_2\text{-(C}_2\text{NO}_4,\text{C}_6,\text{C}_2\text{NO}_4)\text{O}_3$ , is formed simultaneously with binitro-salicylic acid; is only known in combination with oxide of methyl.

*Parasalicyl*. *Parasalicyl* (Paraspiroyl):  $\text{C}_{14}\text{H}_5\text{O}_3$ . If salicylate of copper at  $220^\circ$  be subjected to dry distillation, there goes over with carbonic acid and oxide of carbon a greenish yellow, oily fluid, from which after a little time colorless, transparent crystals are deposited, which have the same constitution as anhydrous salicylous acid. If the oily product of distillation be warmed with dilute potash lye, salicylous acid dissolves, and as residue parasalicyl remains, which, by evaporating the alcoholic solution, crystallizes in quadrilateral prisms; insoluble in water, easily soluble in alcohol and ether; fuses at  $127^\circ$ , forming a pale yellowish fluid, which at  $95^\circ$  stiffens to a radiated crystalline mass; sublims at  $180^\circ$ , in colorless needles. Strong *nitric acid* changes parasalicyl into pikrin-nitric acid. Chlorine and bromine decompose it in the sunlight, forming crystalline products. Towards the alkalis it behaves quite indifferent.

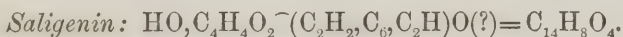
#### PAIRED RADICAL OF SALICYL.

Coumaryl:  $\text{C}_4\text{H}_2\text{-Sa}=\text{C}_4\text{H}_2+\text{O}_2\text{-(C}_2\text{H}_2,\text{C}_6,\text{C}_2\text{H)}=\text{C}_{18}\text{H}_7\text{O}_2$ ; Cou.

Coumarin. *Coumarylous Acid* (Coumarin, Tonka-camphor):  $\text{HO},\text{CouO}$ , is found in the Tonquin bean, in *Asperula odorata*, and in the flowers of *Melilotus off.* The Tonquin beans, which contain this body in crystallized form, are extracted by

alcohol, and the solution evaporated to syrup thickness. It crystallizes from the alcoholic solution in fine, white, lustrous needles, which grate between the teeth; insoluble in cold water, somewhat soluble in boiling, easily soluble in alcohol and ether; heavier than water; possesses a pleasant aromatic smell and burning taste; melts at  $50^{\circ}$ , and stiffens to a crystalline mass; boils at  $270^{\circ}$ . With cold *fuming nitric acid* it gives *nitro-coumarylous acid*, and by being heated with a solution of potassa, it is converted into coumarylic acid, under evolution of hydrogen gas. From the yellow alkaline solution acids again separate coumarin. *Nitro-coumarylous acid* crystallizes from the alcoholic solution in small, white, silky-lustred needles. By continued boiling with nitric acid, it is converted into pikrin-nitric acid.

*Coumarylic Acid*:  $\text{HO}, \text{CouO}_3$ . We boil coumarylous acid with concentrated potassa lye, so long as <sup>Coumarylic acid.</sup> the evolution of gas takes place. The residue is dissolved in water, and the coumarylic acid precipitated by hydrochloric acid. It separates from the boiling alcoholic solution in very lustrous, transparent, bitter-tasting leaflets; reddens litmus, completely saturates the bases, not volatile. Coumarylous, as well as coumarylic acid, when melted with hydrate of potassa, is converted into salicylic acid, under evolution of carburetted hydrogen gas.



*Occurrence*.—In the willow bark a bitter substance occurs, called *Salicin*. By fermentation it separates into sugar and saligenin. Saligenin consists of  $\text{C}_{14}\text{H}_8\text{O}_4$ ; under the influence of oxydizing bodies, it is converted into salicylous acid,  $\text{C}_{14}\text{H}_6\text{O}_4$ , whilst simultaneously water is formed. If we consider saligenin as consisting of  $\text{HO}, \text{C}_4\text{H}_4\text{O}_2 \cdot (\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{O}$ , then its conversion into salicylous acid consists simply in the removal of  $\text{H}_2$  from the pairing.

We obtain saligenin if fifty parts finely pulverized salicin be dissolved in 200 parts water, to the mixture 3 parts emulsin be added, and the whole exposed for 24 hours to a steady temperature of  $40^{\circ}$ . Saligenin generally crystallizes in small rhombohedrons, and is purified by repeated crystallization. From the hot aqueous saturated solution, saligenin crystallizes in rhombic plates, of mother-of-pearl lustre, unctuous to the touch. Dissolves in boiling water in almost every proportion, and in 15 parts water at  $22^{\circ}$ ; also easily soluble in alcohol and ether. If saligenin be heated above  $140$  to  $150^{\circ}$ , it is changed into a yellow, amber-like mass of *saliretin*, which consists of  $\text{C}_{14}\text{H}_6\text{O}_2$ . This substance may also be obtained by the action of dilute <sup>Saliretin.</sup> hydrochloric or sulphuric acid upon saligenin and salicin. It is insoluble in water and ammonia, but dissolves easily in alcohol and ether. Under the influence of *platinum black*, and admission

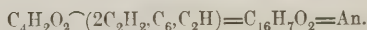
of air, it is converted into *salicylous acid*, even at ordinary temperature; the same oxidation occurs when saliretin is warmed with *chromic acid*, *bichromate of potassa*, or *oxide of silver*. *Concentrated nitric acid* changes it into pikrin-nitric acid. If we let *chlorine* act upon salicin, we obtain several compounds, which consist of sugar united with chlor-, bichlor-, and trichlor-saligenin, and under the influence of emulsin these separate into sugar and the above-mentioned chlorine combinations (*see Salicin*).

*Chlor-saligenin*,  $C_{14}H_7ClO_4$ , crystallizes from the hot aqueous solution in beautiful, colorless, rhombic plates, which dissolve in water, alcohol, and ether. With *potassa saligenin* seems to form a combination. The solution of saligenin and of chlorsaligenin colors the *peroxide of iron salts* blue.

*Rutilin*:  $C_{23}H_{12}O_4$ , and *Rufin*:  $C_{14}H_7O_5$ , are substances obtained by the action of concentrated sulphuric acid upon saligenin (*see Salicin*).

#### SECOND MEMBER.

#### ANISYL:



Anisyl, like salicyl, unites with oxygen to form anisylous and anisylic acid.

*Hydrate of Anisylous Acid*:  $HO, C_4H_2O_2 \cdot (2C_2H_2, C_6H_5)O = HO, AnO$ , forms simultaneously with anisylic acid by the action of nitric acid upon solid anise-oil and dracunculus oil. The mixture obtained by the action of dilute nitric acid is shaken with dilute potassa-lye, which absorbs the anisylic acid, and the remaining fluid anisylous acid is purified by shaking with water and rectification. It is yellow, has an aromatic odor and burning taste; sp. gr. 1.09; boils at  $253^\circ$ ; not easily soluble in water; miscible in all proportions with alcohol and ether. With concentrated *nitric acid*, it gives nitro-anisylous acid, and with *chlorine* and *bromine*, compounds which exhibit anisylic acid, in which 1 atom oxygen is replaced by 1 atom chlorine or bromine. In its behavior to chlorine and bromine, anisylous acid differs widely from salicylous acid. With *ammonia* anisylous acid gives *anisylimidamid*  $= NH_2, An + NH_2, 2An$ , which in its constitution entirely agrees with salicylimidamid; it forms hard, easily pulverized crystals. If anisylous acid be heated with hydrate of potassa, anisylic acid is obtained under evolution of hydrogen gas.

*Hydrate of Anisylic Acid* (Anisic Acid, Draconic Acid):  $HO, AnO_3$ . Solid anise-oil is digested a long time, with moderately concentrated nitric acid, at  $25^\circ$ , and, when the action has ceased, the crude product washed with water, is dissolved in aqueous ammonia. The ammonia salt, obtained by



the evaporation of the aqueous solution, is purified by repeated crystallization, then precipitated by acetate of lead, and the obtained lead-salt decomposed by hydrosulphuric acid. After the decomposition, the whole is treated with boiling water, and from the hot, filtered solution the acid is procured in crystals. Or, we let fall anisyulous acid by drops upon fused hydrate of potassa, dissolve the mass in water, and precipitate the anisylic acid by hydrochloric acid. From dracunculus oil also is anisylic acid obtained by the action of nitric acid. It crystallizes in long, sharp, shining prisms; in cold water is scarcely soluble, but dissolves abundantly in boiling, as also in alcohol and ether. The solution reacts acid; melts at  $175^{\circ}$ ; sublimable. Subjected with baryta to dry distillation anisylic acid separates into anisol and carbonic acid. Treated with *chlorine*, *bromine*, and *nitric acid*, we obtain derived compounds. The *ammonia salt* crystallizes in large, prismatic plates, so do also the *potassa* and *soda salts*. With *oxide of lead* and *oxide of silver* anisylic acid gives not easily soluble salts.

*Bioxychloride of Anisyl*:  $C_4H_2O_2 \cdot (2C_2H_2, C_6, C_2H) \left\{ \begin{matrix} O_2 \\ Cl \end{matrix} = An \right\} \left\{ \begin{matrix} O_2 \\ Cl \end{matrix} \right.$

If we distil anisylic acid with chloride of phosphorus, we thus obtain, under evolution of hydrochloric acid, a distillate, which consists of oxychloride of phosphorus and bioxychloride of anisyl. If this distillate be subjected to repeated distillation, at first, the phosphorus compound goes over, and at  $270^{\circ}$  the anisyl compound. This latter is quickly washed with a little cold water, dried over chloride of calcium, and rectified. A colorless fluid of strong odor; sp. gr. 1.261; boiling point  $262^{\circ}$ ; in the moist air it is quickly converted into anisylic acid, with formation of hydrochloric acid.

*Bioxybromide of Anisyl*:  $C_4H_2O_2 \cdot (2C_2H_2, C_6, C_2H) \left\{ \begin{matrix} O_2 \\ Br \end{matrix} = An \right\} \left\{ \begin{matrix} O_2 \\ Br \end{matrix} \right.$  is obtained by the direct action of bromine upon anisyulous acid. Crystallizes from the etheric solution in white, silky-lusted needles, which do not change in the air, but by being heated with a solution of potassa separate into bromide of potassium and anisylate of potassa. By the continued action of bromine *bioxybromide of bibromanisyl* appears to be formed.

*Anisyl-nitrid*:  $C_{16}H_2O_2 \cdot (2C_2H_2, C_6, C_2H) 3NO_4$ , is formed by the action of nitric acid upon phenetol.

*Bichloranisylic Acid*:  $HO, C_4H_2O_2 \cdot (C_2Cl_2, C_2H_2, C_6, C_2H)O_3$ , is only known in combination with *anisylic acid*. It is formed when dry anisylic acid is exposed to the action of dry chlorine. From the alcoholic solution it crystallizes in fine, shining needles; insoluble in water, easily soluble in warm alcohol and ether; fuses at  $176^{\circ}$ , sublimable.

Derived compounds of anisyl.



*Bromanisylic Acid*:  $\text{HO}, \text{C}_{16}\text{H}_6\text{BrO}_5$ , is, like chloranisylic acid, a double acid, consisting of anisylic and bibromanisylic acid; it is obtained by the direct action of bromine upon anisylic acid. It crystallizes from the alcoholic solution in very fine, shining needles, which fuse at  $204^\circ$ , sublime, and are easily soluble in warm alcohol and ether. With potassa, soda, and ammonia, it gives soluble salts.

*Binitro-anisylic Acid*:  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2(\text{C}_2\text{NO}_4, \text{C}_6\text{C}_2\text{H})\text{O}_3$ , is not known isolated; with anisylic acid it forms two combinations, corresponding to the formulæ:—

1.  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2(\text{C}_2\text{NO}_4, \text{C}_6, \text{C}_2\text{H})\text{O}_3 + 3(\text{HO}, \text{C}_{16}\text{H}_7\text{O}_5) = \text{}^a\text{Nitro-anisylic acid.}$
2.  $\text{HO}, \text{C}_4\text{H}_2\text{O}_2(\text{C}_2\text{NO}_4, \text{C}_6, \text{C}_2\text{H})\text{O}_3 + \text{HO}, \text{C}_{16}\text{H}_7\text{O}_5 = \text{}^b\text{Nitro-anisylic acid.}$

The *former compound* is formed simultaneously with anisylic acid by the action of nitric acid upon dracunculus oil, and is found in the mother liquor which remains behind in the preparation of anisylate of ammonia. It crystallizes from the hot alcoholic solution in flat, colorless, and nearly tasteless needles, hardly soluble in water, easily soluble in alcohol and ether. With *chlorine* and *bromine* it forms *double compounds* of *nitroanisylic* with *chloranisylic* and *bromanisylic acid*.

The *second compound* is obtained when anisylic acid or the preceding compound is digested a long time with concentrated nitric acid. By repeated crystallization from hot alcohol, it appears in very fine, white needles, tasteless and odorless, almost insoluble in cold water, but easily soluble in warm alcohol and ether; melts at  $175$  to  $180^\circ$ , not distillable without decomposition. By boiling *fuming nitric acid*, it is changed into the so-called *binitranisol*, a compound of salicyl-nitrid with nitroanisol. Brought in contact with *chloride of phosphorus*, we obtain, under formation of *bioxychloride of phosphorus*, one of the nitro-compounds  $= (\text{C}_{16}\text{H}_5\text{O}_2, 2\text{NO}_4) \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right\} + \text{An} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right\} (?)$ , corresponding to *bioxychloride of anisyl*; this nitro-compound separates in the air into hydrochloric and nitro-anisylic acid.

*Salt-like Combinations of Oxide of Methyl and Oxide of Ethyl with the Acids of Salicyl and Anisyl.*

*Salicylate of Methyl* (Gaultheric Acid):  $\text{McO}, \text{SaO}_3$ .  
 Combinations of oxide of methyl. This compound is the main constituent of the oil of *Gaultheria procumbens*. If the latter be distilled, at first an oil goes over which consists of  $\text{C}_{10}\text{H}_8$ , and at  $224^\circ$  comes the pure compound. It is also obtained when 2 parts wood-spirit,  $1\frac{1}{2}$  parts salicylic acid, and 1 part sulphuric

acid, are subjected to distillation. A colorless liquid, of pleasant aromatic odor and taste; dissolves a little in water, but in all proportions in ether and alcohol; boils at  $211$  to  $224^{\circ}$ ; sp. gr.  $1.173$ . This compound behaves quite like a paired acid; it expels carbonic acid from its combinations, and forms a series of salts, which contain 1 atom base to 1 atom salicylate of methyl.

The *potassa compound*,  $KO + MeO, SaO_3$ , is obtained by mixing a cold concentrated solution of potassa with salicylate of methyl; it crystallizes from the alcoholic solution in six-sided plates, which are soluble in water, alcohol, and ether. If the aqueous solution be warmed, there are formed wood-spirit and salicylate of methyl. If upon *salicylate of methyl* we let *chlorine* act, we obtain *bichlorosalicylate of methyl*, which crystallizes, and is soluble in alcohol and ether. In the same manner we obtain by bromine the *corresponding bromine* compounds; they possess, like the salicylate of methyl, the properties of an acid, and unite with the bases to form salts. In like manner, by the action of *nitric acid* upon salicylate of methyl, a compound arises, which consists of *binitro-salicylate* and *salicylate of methyl*. If we make use of a mixture of fuming nitric and fuming sulphuric acid, there are formed *binitro-salicylate* and *trinitro-salicylate of methyl*. The former compound crystallizes in pale-yellowish scales, which fuse at  $124^{\circ}$ ; the latter compound crystallizes in yellow plates; they all possess acid properties, and form with ammonia crystallizable salts.

Bichlorosalicylate of methyl.

Bromsalicylate of methyl.

Nitro-salicylate of methyl.

*Anisylate of Methyl*:  $MeO, AnO_3$ , is obtained by distilling 2 parts wood-spirit, 1 part anisyllic acid, and 1 part sulphuric acid. The compound goes over as a heavy oil, which stiffens crystalline. Crystallizes from the alcoholic or etheric solution in white, shining scales, which fuse at  $46^{\circ}$ ; insoluble in water, easily soluble in alcohol and ether; of agreeable odor, like anise oil, burning taste. Gives no compounds with the bases. By *chlorine*, *bromine*, and *nitric acid*, we obtain combinations of oxide of methyl with *chloranisyllic*, *bromanisyllic* and *nitro-anisyllic acid*, all of which are neutral, and crystallize.

Anisylate of methyl.

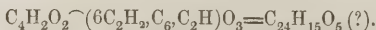
*Salicylate of Ethyl*:  $AeO, SaO_3$ , is obtained, like the oxide of methyl combination. A fluid heavier than water; boils at  $225^{\circ}$ ; smells less agreeably than the methyl compound; behaves like a paired acid. With *chlorine*, *bromine*, and *nitric acid*, it gives the *oxide of ethyl compounds*, which all have the properties of an acid, and crystallize; they correspond to the compounds of *salicylate of methyl*.

Oxide of ethyl compounds.

*Anisylate of Ethyl*:  $AeO, AnO_3$ , a colorless liquid, of burning, aromatic taste and smell; heavier than water, in which it is insoluble; dissolves easily in alcohol and ether; boils at  $250^{\circ}$ ; not acid. Behaves to *nitric acid*, *chlorine*, and *bromine* like the corresponding methyl compound.

## APPENDIX TO THE ACIDS OF THE SALICYL GROUP.

## CARYOPHYLLIC ACID:



Caryophyllic acid.

*Caryophyllic acid* is the principal constituent of the oil of cloves, which is procured from the flower-buds of *Eugenia caryophyllata*. If this oil be subjected to distillation with a concentrated solution of potassa, a neutral oil goes over, whilst caryophyllate of potassa remains; if this substance be decomposed by a mineral acid, caryophyllic acid goes over by distillation. From pimenta oil, which is obtained from the fruit of *Myrtus pimenta*, we obtain, in like manner, *pimentic acid*, which is identical with caryophyllic acid. An oily, water-clear fluid, sp. gr. 1.079, taste aromatic, burning, sharp; odor like cloves; but little soluble in water, easily soluble in alcohol, ether, acetic acid, and fatty oils; boils at  $243^\circ$ , and forms with the bases salts, which have the smell and taste of the acids; by nitric acid it becomes red, and by peroxide of iron salts violet red.

Piment acid.

*Eugenin* is a body which is deposited in leaflets of mother-of-pearl lustre, from the water distilled away from cloves. It is indifferent, easily soluble in alcohol and ether, and has the same constitution as caryophyllic acid.

Eugenin.

*Guaiac acid*. *Guaiac Acid*:  $HO, C_{12}H_7O_5$ . It occurs in guaiac resin. It crystallizes from the etheric solution in irregular warts, dissolves easily in water, alcohol, and ether; is sublimable, and separates by distillation with baryta into carbonic acid and guaiacen  $= C_{10}H_5O_2 (?)$ . As yet not further investigated.

Guaiac acid.

*Fourth Group.*

Carbon Nucleus:  $C_8$ .

It includes:

- a. *The Benzid Group*: Component  $C_2H_2$ ; Nucleus  $C_8$ ; Active element H.
- b. *The Benzoyl Group*: Component  $C_2H_2$ ; Nucleus  $C_8$ ; Active part  $C_2H$ .

## THE BENZID GROUP.

Component  $C_2H_2$ ; Nucleus  $C_8$ ; Active element H.

The benzid group corresponds to the methyl group; thus, for example, ethyl,  $2C_2H_2, H$ , with the nucleus  $C_8$ , is the radical of benzin  $2C_2H_2, C_8, H$ .

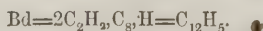
To this group belong :

		Boiling point.
Member 1.	(unknown).	
" 2.	Benzid, Bd = $2C_2H_2, C_8, H=C_{12}H_5$	— 80°.5.
" 3.	Tolid, Td = $3C_2H_2, C_8, H=C_{14}H_7$	— 109°.
" 4.	Xyloid, Xd = $4C_2H_2, C_8, H=C_{16}H_9$	— —
" 5.	Cumid, Cd = $5C_2H_2, C_8, H=C_{18}H_{11}$	— 144°.
" 6.	Cymid, Cyd = $6C_2H_2, C_8, H=C_{20}H_{13}$	— 171°.

The radicals of this group are not known in isolated condition; they all combine with H, and these combinations correspond to 4 volumes gas. Each member of the benzid group has a corresponding one in the benzoyl group; thus benzoyl  $2C_2H_2, C_8, C_2H$  corresponds to benzid  $2C_2H_2, C_8, H$ , and benzoic acid  $HO(2C_2H_2, C_8, C_2H)O_3$  to hydro-benzid  $(2C_2H_2, C_8, H)H$ , in the same manner as acetic acid  $HO(C_2H_2, C_2H)O_3$  corresponds with hydro-methyl  $(C_2H_2H)H$ . As by the decomposition of hydrate of acetic acid hydro-methyl arises, so from the hydrate of benzoic acid is formed hydro-benzid, from toluylic acid, hydro-tolid, etc. The hydrogen compounds of this group also arise by the dry distillation, especially of carboniferous organic bodies. The radicals farther unite with chlorine, bromine, and  $NO_4$ . Thus, by the action of chlorine upon hydro-benzid  $(C_{12}H_5)H$ , we first obtain  $(C_{12}H_5)Cl$ , but if the action of chlorine continue, we obtain  $(C_2H_2, C_8, C_2H)Cl_3$ . As soon as these bodies form, they unite with the simultaneously arising hydrochloric acid, hence we obtain  $(C_{12}H_3)Cl_3 + 3HCl$ ; if we treat this compound with potassa lye, it separates into  $(C_{12}H_3)Cl_3$ , chloride of potassium and water. It may be supposed that by the continued action of potassa upon  $(C_{12}H_3)Cl_3$  an acid arises, which is constituted of  $(C_{12}H_3)O_3$ . If we treat the nitrogen-combinations of these radicals with hydro-sulphuric acid,  $NO_4$  is replaced by  $NH_2$  (under separation of sulphur and formation of water), whereby organic bases arise, which appear as ammonia, in which the third atom of hydrogen is replaced by  $C_{12}H_5, C_{14}H_7$ , etc., and which correspond to the bases of the methyl group (compare General Part, page 81).

#### SECOND MEMBER.

#### BENZID:



*Hydrobenzid* (Benzin, Benzol):  $BdH$ . Occurs in oil gas, in coal-tar, and is formed, when the vapor of bergamot-oil is led through a glowing tube filled with pieces of lime. It farther arises by the decomposition of hydrate of benzoic acid and of cinnamic acid, generally of all bodies which go over into benzoic acid by the dry distillation of phthalinic acid, etc. A mixture of 1 part



hydrate of benzoic acid with 3 parts hydrate of lime is exposed in a retort to a slowly increasing heat. The benzin, which goes over with water, is separated from the latter, and distilled a few times over potassa-lye. Or, we distil coal-tar, subject the part, which goes over first and swims upon the water, to fractional distillation, and collect the part which goes over between 80 and 90°. The distillate is cooled to  $-12^{\circ}$ , benzin is solid, and can, by expression, be divided from the yet fluid portion (in continued distillation of the just mentioned fluid at 100 to  $115^{\circ}$  *tolin* goes over, at 140 to  $144^{\circ}$  *cumin* goes over, and at 170 to  $175^{\circ}$ , probably *cymen*). Benzin, at common temperature, is a clear, colorless fluid, strongly refracting light; pleasant, etheric odor; under  $0^{\circ}$  it stiffens to a crystalline mass, and at  $+7^{\circ}$  becomes again fluid; little soluble in water, easily soluble in alcohol and ether; boils at  $80^{\circ}.5$ ; sp. gr. 0.85. By fuming nitric acid we obtain, first *nitro-benzid*  $= (2C_2H_2, C_8, H)NO_4$ , and, by farther action, a combination of nitro-benzid with  $(C_2H_2, C_8, C_2H)3NO_4$ , or the so-called *binitro-benzid*. Chlorine leads benzin first into  $(2C_2H_2, C_8, H)Cl + HCl$ , and then into  $(C_2H_2, C_8, C_2H)Cl_3 + 3HCl$ . With *concentrated sulphuric acid* we obtain sulphobenzid  $Bd, SO_2$ , and sulphobenzid-sulphuric acid  $HO(Bd, SO_2)^-SO_3$  corresponding to sulph-ethyl-sulphuric acid.

*Chloride of Benzid*:  $BdCl$ , is not known isolated.

*Azobenzid*.

*Azobenzid*:  $BdN$ , is obtained, when an alcoholic solution of nitrobenzid is distilled with an alcoholic solution of potassa; towards the end of the operation a red body goes over, which stiffens in larger crystals, and from the etheric solution is obtained in beautiful perfect crystals, which fuse at  $65^{\circ}$ , boil at  $193^{\circ}$ , and volatilize undecomposed.

*Azoxybenzid*.

*Azoxybenzid*:  $C_{12}H_5NO = BdNO = BdO_2 + BdN_2$ . If to a solution of nitrobenzid, in 10 parts alcohol, we add gradually as much potassa as the nitrobenzid used, and after decomposition has taken place, distil the fluid, a residue remains in the retort, which consists of 2 layers; the upper one after a short time stiffens to oily, yellow, lustrous, quadrangular prisms, which are pulverizable, and fuse at  $36^{\circ}$ . This is azoxybenzid (simultaneously is also formed anilin  $NH_2, C_{12}H_5$ ). If we boil this body a little while with not-fuming nitric acid, small yellow prisms consisting of  $(C_{24}H_9NO_4)N_2O_2$ , called *nitro-azoxybenzid*, are separated from the nitric acid solution; if upon this substance we let an alcoholic potassa solution act, we obtain a red crystalline powder consisting of  $C_{24}H_9N_3O_2$ . If we treat azobenzid with fuming nitric acid, until there is a reaction, red crystals form in cooling, which, after being washed with dilute nitric acid and water, separate from the alcoholic solution in flat-pressed crystals; this body consists of  $(C_{24}H_9NO_4)N_2 = (C_{12}H_5)N + (C_{12}H_4NO_4)N$ . If we boil azobenzid with fuming nitric acid for a few minutes,

we obtain red needles, which consist of  $(C_{24}H_8, 2NO_4)N_2 = (C_{12}H_5)N + (C_{12}H_3, 2NO_4)N$ , and are called *binitro-azobenzid*. This body gives with sulphide of ammonium an organic base—*delphenin*,  $= C_{12}H_6N_2 = (C_{12}H_4N)NH_2$ .

*Nitrobenzid*:  $Bd + NO_4$ . To moderately concentrated nitric acid benzin is added in small quantities, and from the mixture the nitro-benzid is precipitated by water. It is also formed by the dry distillation of nitro-benzoic acid salts. A yellowish fluid, of penetrating, sweet taste, and odor like cinnamon oil; sp. gr. 1.209; boils at  $213^\circ$ ; crystallizes at  $-3^\circ$ ; insoluble in water, but miscible in every proportion with ether and alcohol. If into an alcoholic solution of nitro-benzid mixed with a little hydrochloric acid we bring some zinc, or if we mix the alcoholic solution with sulphide of ammonium, we thus obtain *anilin* (benzidam)  $NH_2Bd$ , in the latter case sulphur is separated. If nitro-benzid be treated with a mixture of fuming sulphuric and fuming nitric acid, the so-called *binitro-benzid* is formed, which consists of *nitrobenzid*  $+ (C_2H_2, C_8, C_2H)3NO_4$ .

*Sulpho-benzid*:  $Bd + SO_2$ . If to anhydrous sulphuric acid we add benzin, and dilute the glutinous mass with water, after a little time sulpho-benzid is precipitated, and in the solution sulpho-benzid sulphuric acid, and free sulphuric acid are found, and are separated in the ordinary way by baryta. From the alcoholic or etheric solution sulpho-benzid is separated in determinable crystals, which fuse at  $100^\circ$ , in higher temperature volatilize, and are insoluble in water, but dissolve easily in alcohol and ether.

*Sulpho-benzid-sulphuric Acid*:  $HO(Bd, SO_2)^-SO_3$ . Forms a crystalline mass, which is decomposed in a higher temperature. Gives with *ammonia*, *potassa*, *soda*, and *oxide of zinc* pure crystallizable salts. The compound with oxide of copper appears in beautiful perfect crystals, which contain water.

#### PAIRED COMBINATIONS OF BENZID.

1. *Picramyl*:  $Per = C_2H, \neg Bd = C_{12}H_5 \neg C_2H$ .

Pairling  $C_2H$ ; Component  $2C_2H_2$ ; Nucleus  $C_8$ ; Active element  $H = C_{14}H_6$ .

*Picramyl* (Stilbene) occurs in combination with oxygen in bitter almond oil. It is probably a paired radical, in which benzid assumes the place of pairling, and  $C_2H$  appears as active part; if the active H leaves benzid, and  $C_2H$  takes its place, then picramyl is converted into benzoyl  $2C_2H_2, C_8, C_2H = C_{14}H_5$ . Picramyl is known by itself and in combination with O, Cl, S, and N.

*Pure picramyl* is obtained when sulphide of picramyl  $PerS_2$  is heated in a retort; it evolves sulpho-carbonic acid and hydro-sulphuric acid, and a residue remains which consists of picramyl and thionessal. If, after the evolution of gas has ceased, this re-

sidue be strongly heated, at first picramyl goes over. It is repeatedly crystallized out of alcohol and then out of ether; forms pointed, rhombic, colorless, and tasteless leaflets, of mother-of-pearl lustre, which dissolve more easily in ether than in alcohol. From the melted state, by being severely shaken, it becomes solid; boils at  $292^{\circ}$ ; distilled with dilute chromic acid, it gives bitter almond oil; combines directly with *chlorine* and *bromine*.

*Oxide of Picramyl* (Bitter Almond Oil):  $\text{PerO}_2$ .  
Bitter almond oil. Bitter almond oil is formed by the so-called bitter

almond oil fermentation, which consists of the decomposition of amygdalin, occurring in bitter almonds, under the influence of emulsin and water, into bitter almond oil, sugar, and hydrocyanic acid. It is also formed by the action of nitric acid upon cinnamon oil, by distillation of benzoin resin with nitric acid, by oxidation of styracin, etc. We obtain it when bitter almonds, which have been freed from fatty oils by expression, are ground with water to an emulsion, the mass digested for 12 to 24 hours at  $30$  to  $40^{\circ}$ , and then distilled in a vapor apparatus. Instead of bitter almonds we may use the stones of cherries, peaches, apricots, and the leaves of the laurel, also the bark of *Prunus Padus*. The obtained bitter almond oil, containing hydrocyanic acid, which is collected upon the bottom of the vessel, is intimately mixed with lime-water and a solution of protochloride of iron, and then rectified. Colorless, thin-flowing, peculiar fluid, of pleasant, aromatic odor, and sharp, burning taste. Dissolves in 30 parts water, mixes with alcohol and ether in all proportions, boils at  $176^{\circ}$ , sp. gr. 1.043. In concentrated nitric acid and sulphuric acid it is, in the cold, soluble without decomposition.

If we let bitter almond oil stand with *potassa lye* a little while, in a closed vessel, it is changed into *benzoin*  $\text{C}_{28}\text{H}_{12}\text{O}_4$ . The same change follows very quickly by using an alcoholic solution of potassa or cyanide of potassium. Benzoin behaves to bitter almond oil as anisoil to anise oil, or metaldehyd to aldehyd. If 2 atoms bitter almond oil unite to form a common atom, under separation of 1 atom H, we thus obtain *stilbyl*  $\text{C}_{28}\text{H}_{11}\text{O}_4$ , which may be considered as a paired compound of bitter almond oil with benzoylous acid  $(\text{C}_{14}\text{H}_6\text{O}_2)$ ,  $(\text{C}_{14}\text{H}_5\text{O}_2)$ , and if 2 atoms hydrogen leave benzoin we obtain *benzil*  $\text{C}_{28}\text{H}_{10}\text{O}_4$ .

Benzoin.

*Benzoin* forms clear, very lustrous and white crystals, which are prismatic, and destitute of odor and taste; at  $120^{\circ}$  they melt to a colorless liquid, which, in cooling, stiffens to a large-leaved radiated mass; quite volatile, insoluble in water, soluble in alcohol; if the alcoholic solution be shaken with ammonia, we obtain *benzoinamid*  $\text{N}_4 + 3\text{C}_{23}\text{H}_{12}$ . If we let the solution, saturated with ammonia gas, stand for several months, we obtain *benzoinam*,  $(\text{C}_2\text{H}_{12})\text{O}_2 + (\text{C}_{23}\text{H}_{12})\text{N}_2$ , with several other



products. *Benzoinamid* crystallizes in silky, fusible, volatile needles; tasteless and odorless; insoluble in water, not easily soluble in alcohol and ether. *Benzoinam* appears in white, odorless, microscopic needles, which, upon addition of a little hydrochloric acid, dissolve easily in alcohol. *Stilbyl*,  $C_{28}H_{11}O_4$ , is obtained when upon bitter almond oil moist chlorine gas acts. Crystallizes in direct prisms, resembles very much benzoin, and combines with potassa.

*Benzil*:  $C_{28}H_{10}O_4$ , is formed when benzoin is treated with concentrated sulphuric acid and moist chlorine gas; from the etheric solution it crystallizes in transparent, six-sided columns, an inch in length; tasteless and odorless; insoluble in water, easily soluble in alcohol and ether; fusible and sublimable. If a hot alcoholic solution of benzil be mixed with aqueous ammonia, we obtain *azobenzil*,  $N_2 + 3C_{28}H_{10}O_2$ . If into the warm solution of benzil in anhydrous alcohol ammonia gas be led, thus are formed *imabenzil*,  $NH, C_{28}H_{10}O_2$ , which is almost insoluble in boiling alcohol and ether; *benzilimid*,  $NH, C_{28}H_{10}O_2$ , isomeric with imabenzil, not easily soluble in alcohol and ether, and *benzilam*,  $N + C_{28}H_9$ , which is easily dissolved in those fluids. If we boil stilbyl with a concentrated alcoholic solution of potassa so long as a proof is completely dissolved in water, there is found in the solution benzilate (stilbylate) of potassa. If we boil this substance with dilute hydrochloric acid, whilst cooling, *benzilic acid*,  $HO, C_{28}H_{11}O_5 = HO(C_{14}H_6O_2)(C_{14}H_5)O_3$ , is separated in shining needles, which are easily soluble in alcohol, but not easily in water; if we heat benzilic acid with *chloride of phosphorus*, we obtain  $HO, C_{28}H_{10}ClO_3$ .

Bitter almond oil, exposed to the air, is converted by absorption of oxygen into hydrate of benzoic acid  $(2C_2H_2, C_8, H)(C_2H)O_2 + O_2 = HO, (2C_2H_2, C_8, C_2H)O_3$ . If we conduct this substance through a glowing tube, we obtain oxide of carbon and benzin. If *bitter almond oil* be brought in contact with *concentrated aqueous ammonia*, after a little time crystals of nitro-picramyl  $N_2 + 3Pcr$  are deposited; if we use the crude bitter almond oil instead of the pure, different products are formed, as *nitro-picramyl*, *benzhydramid*, *amarin* (a base), all of which consist of  $N_2 + 3C_{14}H_5$ ; also *benzoylazotid*,  $NC_{14}H_5$ , and *azobenzoyl*,  $N_2 + 3C_{14}H_5$ . Besides these, there are yet obtained *azobenzoid*, *azobenzoidin*, *azobenzoidil*, all of which correspond to the formula  $N, C_{28}H_{11} + 2(N_2, C_{28}H_{11})$ , and *benzamil*  $N_2 + (C_{28}H_{10})O_2$ , *pikryl*  $N + (C_{42}H_{15})O_4$ . Pure bitter almond oil, brought in contact with *hydrosulphuric acid*, forms *sulphide of picramyl*. If we use *sulphide of ammonium*, we thus obtain simultaneously with sulphide of picramyl, more nitrogen combinations, which unite with sulphide of picramyl, thus:  $3PcrS_2 + N_4, Pcr_3$  and  $6PcrS_2 + N_2, Pcr_3$ . If we treat bitter almond oil with *chloride of phosphorus*, we obtain *chloride of picramyl*  $PcrCl_2$ ,



and if upon this we let *sulpho-carbonic acid* in common with *ammonia* act, thus is formed *sulpho-cyanide of benzoyl*,  $C_{14}H_5, CyS_2$ .

*Sulphide of Picramyl*:  $PcrS_2$ , arises by the action of hydrosulphuric acid upon bitter almond oil. A white powder, not crystalline; insoluble in water and alcohol; imparts to the skin a garlic odor. Brought in contact with ether, it is instantaneously fluid; transparent, and is dissolved in small quantity; if we add to the ether only a few drops of alcohol, it becomes at once solid again. Fuses at  $91$  to  $95^\circ$ , and stiffens, after cooling, to a crystalline mass. If it be any time preserved in fused state, it separates, under evolution of carbonic

Thionessal. and hydrosulphuric acid, into picramyl and *thionessal*:  $C_{12}H_3(C_{14}H_6)S=C_{26}H_9S$ , which distils over, when picramyl has volatilized. *Thionessal* is colorless, odorless, crystallizes in silky lusted needles, scarcely soluble in boiling alcohol and ether, but is absorbed in considerable quantity by boiling naphtha; it melts at  $178^\circ$ , and volatilizes undecomposed; boiled with *nitric acid*, it goes over into *nitro-thionessal*,  $C_{26}H_7, 2NO_4, S$ ; and, in the same manner, by the action of bromine, we obtain *bromthionessal*  $= C_{26}H_7Br_2S$ , which is insoluble in alcohol, ether, water, and naphtha; in a higher temperature it melts, and in cooling stiffens in rhombic plates, and suffers itself to volatilize undecomposed. If we treat sulphide of picramyl with an alcoholic solution of potassa, we obtain sulphide of potassium, and bitter almond oil. With *sulphide of ammonium*, sulphide of picramyl unites, forming  $2(NH_4S) + 3PcrS$  (see below Nitro-picramyl).

*Chloride of Picramyl*:  $PcrCl_2$ , is obtained when bitter almond oil is distilled with chloride of phosphorus, under simultaneous formation of bioxychloride of phosphorus. Colorless transparent liquid, of penetrating odor; insoluble in water, dissolves easily in alcohol and ether; sp. gr. 1.245. Gives, with an alcoholic solution of sulphide of potassium and hydrogen,  $KS, HS$ , chloride of potassium and sulphide of picramyl. A compound of *bichloride of picramyl* with picramyl  $= Pcr + PcrCl_2$ , or, *proto-chloride of picramyl*:  $PcrCl$ , is obtained when over fused picramyl chlorine gas is conducted, until it evolves vapor of hydrochloric acid. If the mass be treated with cold ether, a part is dissolved; the part soluble in ether as well as the insoluble part has the same constitution. The latter dissolves in boiling ether, and by spontaneous evaporation is separated in small, transparent, oblique-prismatic crystals. If the solution in cold ether be mixed with alcohol, and left to spontaneous evaporation, octagonal transparent plates form, which dissolve easily in alcohol and ether. If we boil both combinations in an alcoholic solution of potassa, we obtain chloride of potassium, and compounds which

Protochloride of picramyl.

*Chloride of Picramyl*:  $PcrCl_2$ , is obtained when bitter almond oil is distilled with chloride of phosphorus, under simultaneous formation of bioxychloride of phosphorus. Colorless transparent liquid, of penetrating odor; insoluble in water, dissolves easily in alcohol and ether; sp. gr. 1.245. Gives, with an alcoholic solution of sulphide of potassium and hydrogen,  $KS, HS$ , chloride of potassium and sulphide of picramyl. A compound of *bichloride of picramyl* with picramyl  $= Pcr + PcrCl_2$ , or, *proto-chloride of picramyl*:  $PcrCl$ , is obtained when over fused picramyl chlorine gas is conducted, until it evolves vapor of hydrochloric acid. If the mass be treated with cold ether, a part is dissolved; the part soluble in ether as well as the insoluble part has the same constitution. The latter dissolves in boiling ether, and by spontaneous evaporation is separated in small, transparent, oblique-prismatic crystals. If the solution in cold ether be mixed with alcohol, and left to spontaneous evaporation, octagonal transparent plates form, which dissolve easily in alcohol and ether. If we boil both combinations in an alcoholic solution of potassa, we obtain chloride of potassium, and compounds which

correspond to the formula  $C_{28}H_{11}Cl$ , consequently consist of *stilbyl* and *chlorine*; both are oily bodies, and are precipitated by water from the alcoholic solution; these compounds take 2 atoms more of chlorine and form a body not easily soluble in ether, which forms small lenticular crystals. If we bring the oily substance in contact with bromine, we obtain  $C_{28}H_{11}Br_2Cl$ . Protochloride of stilbyl.

*Protobromide of Picramyl*:  $PerBr$ , is obtained by the action of bromine upon picramyl; a white powder, insoluble in ether and alcohol.

*Nitro-picramyl* (Hydrobenzamid):  $Per_3N_2$ . Aqueous ammonia is left in contact with pure bitter almond oil for 6 or 8 days; crystals of nitro-picramyl are separated, which are obtained from the alcoholic solution in octahedrons, destitute of color, smell, and taste; insoluble in water, easily soluble in alcohol and ether; melts at  $110^\circ$ , and becomes solid again after a few days; in contact with acids it separates with addition of water into ammonia and bitter almond oil. By *dry distillation* ammonia first escapes, and a light, fluid, fragrant oil. When the evolution of ammonia has ceased, a melted mass is found in the retort, which stiffens crystalline; it consists of two substances; one is soluble in ether, and crystallizes in shining leaflets; the other is insoluble in ether; it is a base, *lophin*, consisting of  $N_2C_{46}H_{17}$ . If we melt *nitro-picramyl* with *hydrate of potassa*, ammonia escapes, and a residue remains, which after being leached with water consists of *benzostilbin* and *benzolon*; the former is soluble in alcohol. If to its alcoholic solution we add some drops of hydrochloric acid, *benzostilbin* is separated in small white crystals; it either consists of  $C_{16}H_6O$  or of  $C_{31}H_{11}O_2$ . The *benzolon* insoluble in alcohol is dissolved by concentrated sulphuric acid with splendid red color; if we add alcohol to the solution, it is precipitated as a crystalline powder, insoluble in water and alcohol; it fuses at  $248^\circ$ ; sublimes unchanged, and consists of  $C_{22}H_8O_2$ . If into the alcoholic solution of nitro-picramyl we conduct *hydrosulphuric acid*, sulphide of ammonium is formed, and a white mealy powder, which consists of 2 atoms sulphide of ammonium and 3 atoms sulphide of picramyl, and is called sulpho-hydrobenzoyl (*see above* Sulphate of Picramyl). Nitro-picramyl.  
Benzostilbin and benzolon.

If we boil nitro-picramyl a few hours with a *pure solution of potassa*, it is converted into a base, *amarin* (benzolin), which is metameric with nitro-picramyl.

*Benzhydramid*, which is constituted like nitro-picramyl, is formed simultaneously with that substance and *amarin*, by the action of ammonia upon crude bitter almond oil; it crystallizes in colorless, tasteless, and inodorous Benzhydramid.

prisms, but it gives with hydrochloric acid neither ammonia nor bitter almond oil.

Paired compounds of oxide of picramyl.

*Picramyloxyd-Sulphuric Acid.* By the action of anhydrous sulphuric acid upon bitter almond oil, we obtain a glutinous mass; if it be diluted with water, and saturated with baryta, a baryta salt remains

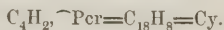
dissolved.

*Picramyloxyd-Formic Acid:*  $\text{HO}(\text{PcrO}_2)\text{FoO}_3$ , is obtained when a saturated aqueous solution of bitter almond oil, which contains hydrocyanic acid, is mixed with hydrochloric acid, and evaporated to dryness. The residue consists of chloride of ammonium, benzamid, and picramyloxyd-formic acid, which latter is extracted by ether. After the evaporation of the etheric solution, we obtain picramyloxyd-formic acid in crystals; it tastes rather strongly acid, and smells a little like bitter almonds. With oxidizing bodies it gives benzoic acid, carbonic acid, and water. With the bases it forms completely neutral salts. It withdraws carbonic acid from its combinations.

Benziminic acid.

*Benziminic Acid.* If we let an alcoholic solution of bitter almond oil, saturated with ammonia, stand for 28 hours, and then mix it with water, there remains dissolved benziminate of ammonia. Hydrochloric acid separates the acid; silky snowy crystals, insoluble in water, not easily soluble in alcohol; melts in the heat, and is decomposed by distillation.

#### CINNAMYL:



Cinnamyl.

Cinnamyl is a paired radical, which consists of picramyl with the pairling  $\text{C}_4\text{H}_2$ . In its combining proportions it quite agrees with picramyl. It is not known isolated; it is formed by the decomposition of cinnamon oil. By the distillation of Java, Ceylon, and Chinese cinnamon, as well as cassia buds, with water, volatile oils are procured, which, in respect to color and odor, differ widely from each other, but in their constitution and chemical relations present no differences. This oil, which is called cinnamon oil, consists of  $\text{C}_{20}\text{H}_{11}\text{O}_2$ , and may be considered as a paired combination of methyl with oxide of cinnamyl  $= \text{C}_2\text{H}_3, \text{C}_{18}\text{H}_8\text{O}_2$ . Cinnamon oil absorbs oxygen from the air. There are formed two resins and oxide of cinnamyl. If we treat the latter with a concentrated solution of potassa, or with nitrous acid, it is converted into bitter almond oil, whilst the pairling  $\text{C}_4\text{H}_2$  is separated.

Oxide of cinnamyl.

*Oxide of Cinnamyl:*  $\text{CyO}_2 = \text{C}_4\text{H}_2(2\text{C}_2\text{H}_2, \text{C}_8, \text{H})\text{C}_2\text{H}_3\text{O}_2$ , is found in old cinnamon oil, by the distillation of which it is obtained; or, we dissolve



nitrate of cinnamyl (*see below*) in water, whereby oxide of cinnamyl is precipitated. It is washed a few times with water, then distilled with water, and dried over chloride of calcium. A colorless fluid, of pleasant cinnamon odor. Exposed to the air, it is converted completely into cinnamic acid,  $\text{HO}(\text{C}_{18}\text{H}_{17})\text{O}_3$ . If we heat it with *nitric acid*, we thus obtain benzoic acid and nitro-benzoic acid. If we distil the latter with a concentrated solution of potassa, it is converted, under evolution of hydrogen gas, into bitter almond oil, whilst simultaneously more benzoic acid is formed. Brought in contact with *ammonia gas*, we obtain *nitro-cinnamyl*.

*Nitrate of Cinnamyl*:  $\text{CyO}_2\text{NO}_5$ , is procured either by direct union, or by dropping cinnamon oil into concentrated nitric acid. A solid crystalline mass, soluble in alcohol and ether, which, in contact with water, separates into oxide of cinnamyl and nitric acid. If into an aqueous solution of oxide of cinnamyl *iodide of potassium* and *iodine* be brought, there is formed a crystalline, bronze-colored precipitate; soluble in alcohol and ether; it consists of  $3\text{CyO}_3 + \text{I}_3 + \text{KI}$ .

*Sulphide of Cinnamyl*:  $\text{CyS}_5$  is obtained, if into an alcoholic solution of nitro-cinnamyl hydrosulphuric acid be led. Quite resembles sulphide of picramyl.

*Oxychloride of Chlorcinnamyl*:  $\text{C}_{18}\text{H}_4\text{O}_2\text{Cl}_4 = \text{C}_4\text{H}_2(\text{C}_{14}\text{H}_2\text{Cl}_4)\text{O}_2$ , is obtained by the action of chlorine upon oxide of cinnamyl. Sublimes in white needles.

*Nitro-cinnamyl*:  $\text{Cy}_3\text{N}_2$ , crystallizes in direct prisms, colorless, inodorous, insoluble in water, melts, and stiffens to a transparent mass. Upon this, *hydrochloric acid* and *potassa* are without action. It is obtained by the action of ammonia upon oxide of cinnamyl.

*Cinnamon Oil*:  $\text{C}_2\text{H}_3, \text{CyO}_2$ , possesses generally a yellow color, a pleasant cinnamon odor, and sweet burning taste; sp. gr. 1.035; is solid below  $0^\circ$ ; in water not easily soluble, but easily so in alcohol and ether. Exposed to the air, it absorbs oxygen, and separates into cinnamic acid, and two *resins*, one of which is said to consist of  $\text{C}_{12}\text{H}_5\text{O}$ , the other of  $\text{C}_{30}\text{H}_{15}\text{O}_4$ . *Hydrochloric acid gas* also decomposes cinnamon oil, forming various resins and some volatile oils. *Cassia-bud oil* is said to form with *ammonia gas* an acid and a neutral compound  $= \text{NH}_3, \text{C}_{20}\text{H}_{11}\text{O}_2$ , and  $\text{NH}_3, 2\text{C}_{20}\text{H}_{11}\text{O}_2$ .

*Cinnamein* (Stiracin):  $\text{C}_{36}\text{H}_{16}\text{O}_4$ . This substance is found in storax, in Peruvian and Tolu-balsam, in common with cinnamic acid and various resins. Cinnamein behaves to oxide of cinnamyl as benzoin to bitter almond oil. This substance is procured from Peruvian balsam, when an alcoholic solution of the balsam is mixed with an alcoholic solution of potassa so long as a precipitate of resin-potassa is formed. If the alcoholic solution, separated from this precipitate, be mixed with water, cinnamein is separated in the form of an oil. A pale, reddish-brown fluid, heavier than water, inodorous, almost tasteless,

Appendix to  
oxide of cinna-  
myl.

Cinnamein.



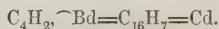
insoluble in water, soluble in alcohol and ether; boils at  $305^{\circ}$ ; volatile, burns with a very sooty flame. If it be decomposed with dilute potassa lye, it is separated into cinnamic acid and peruvín; heated with hydrate of potassa, it forms, under evolution of hydrogen gas, cinnamate of potassa.

*Metacinnamein*:  $C_{36}H_{16}O_4$ . This substance occurs in dissolved cinnamein, and is separated when the latter is cooled under  $0^{\circ}$ . It is generally found in fluid storax. Forms beautiful, white, ciliary crystals; insoluble in water; it dissolves in 3 parts boiling, 20 parts cold alcohol, and 3 parts ether; it melts in hot water, forming an oily liquid, which, after cooling, stiffens crystalline. In contact with potassa, it separates like cinnamein into peruvín and cinnamic acid. Treated with *chlorine*, it gives a substance consisting of  $C_{36}H_{12}Cl_4O_4$ .

*Peruvín*. *Peruvín* (Styracon):  $C_{18}H_{12}O_2$ . Oily, of pleasant odor; little soluble in water; volatile; mixes with alcohol and ether in all proportions.

*Styron*. *Styron*:  $C_{18}H_{10}O_2$ , may be obtained, when cinnamein is distilled with a strong solution of potassa. It is separated from the milky distillate in long silky needles; odor agreeable; melts at  $33^{\circ}$ ; sublimes; in water somewhat soluble, easily so in alcohol and ether. By being distilled with peroxide of manganese and sulphuric acid, it gives bitter almond oil.

## 2. CINNAMID:



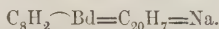
*Cinnamin*. *Hydro-cinnamid* (Cinnamin, Styrol):  $\text{CdH} = (C_4H_2 \cdot \text{Bd})H$ , is obtained by dry distillation of cinnamic acid  $\text{HO} \cdot (C_4H_2 \cdot \text{C}_{14}H_5)O_3$ , with hydrate of lime. It is also found in storax, and is formed by distillation of that substance with water and carbonate of soda. Colorless, transparent, very mobile fluid, of peculiar aromatic odor, resembling that of benzín, with burning taste. Slightly soluble in water, easily soluble in alcohol and ether; by warming dissolves sulphur, which by cooling is deposited in large crystals. Boils at  $144^{\circ}$ ; sp. gr. 0.924. If cinnamein be heated for half an hour upon the oil bath to  $200^{\circ}$ , it is converted into a solid, hard, colorless substance, which becomes soft by warming; is insoluble in water and alcohol, and only in a scanty portion soluble in ether; and by heating in a retort is again converted into fluid cinnamin. This body is called *metacinnamin* (metastyrol), and consists of  $C_{14}H_7$ ; consequently, 7 atoms cinnamin give 8 atoms metacinnamin. If metacinnamin be treated with *fuming nitric acid*, we obtain *nitro-metacinnamin*, as a white, completely amorphous powder, insoluble in water, alcohol, and ether, and  $= (C_{14}H_6)NO_4$ . If cinnamin be treated with *fuming nitric acid*, we obtain *nitro-cinnamin*  $= (C_4H_2 \cdot \text{Bd})NO_4$ ; if it be boiled with dilute nitric

acid, we obtain nitro-cinnamin, benzoic acid, nitro-benzoic acid, and bitter almond oil, under evolution of carbonic acid. *Chromic acid* quickly converts cinnamin into benzoic acid. By the action of *chlorine* and *bromine*, we obtain chlorcinnamin and bromcinnamin.

*Bromcinnamin*:  $C_{16}H_8Br_2 = (C_4H_2, \curvearrowright Bd)Br + HBr$ , is obtained if bromine be dropped into cinnamin so long as it is absorbed without evolution of hydrobromic acid. Crystallizes from the alcoholic solution; insoluble in water, easily soluble in alcohol and ether, of not disagreeable odor, exciting a flow of tears; melts at  $62^\circ$ ; boils at  $230^\circ$ . Brought together with an alcoholic solution of potassa, it gives bromide of potassium and  $(C_4H_2, \curvearrowright Bd)Br = C_{16}H_7Br$ .

*Nitrocinnamin*:  $(C_4H_2, \curvearrowright Bd)NO_4$ , is obtained by the action of fuming nitric acid upon cinnamin. Separates from the hot alcoholic solution in magnificent rhombic prisms; smells like oil of cinnamon, exciting tears; produces blisters. Gives with an alcoholic solution of potassa *nitro-cinnamid*  $(C_4H_2, \curvearrowright Bd)N$ , corresponding to nitrobenzid.

### 3. NAPHTHALID:



Naphthalid relates to benzid as does cinnamid. The pairing of naphthalid is  $C_8H_2 = 2C_4H$ . It is found in combination with hydrogen as *naphthalin*  $NaH$ , in coal tar, and is generally produced by dry distillation of most organic bodies, when they are exposed to a very high temperature.

*Hydronaphthalid* (Naphthalin):  $NaH = (C_8H_2, \curvearrowright C_{12}H_5)H = C_{20}H_8$ . We procure naphthalin readily by Hydronaphthalid. distillation of coal tar, but its quantity is considerably enlarged if chlorine be led into the tar, or if the latter be treated with chloride of lime, water, and sulphuric acid. Naphthalin always goes over last by distillation of tar, mixed, however, with anthracin, from which it is separated by treatment with alcohol, in which anthracin is insoluble. Both bodies are deposited if the distillate be cooled to  $-10^\circ$ . Naphthalin is purified by recrystallization from the hot alcoholic solution. Crystallizes by slow evaporation in thin, white, rhombic leaflets, and by slow sublimation in white, extremely light flakes, of peculiar odor and burning aromatic taste; insoluble in water, easily soluble in alcohol, ether, acetic acid, and a solution of oxalic acid; melts at  $79^\circ$ ; boils at  $212^\circ$ ; sp. gr. 1.045. Easily distils with vapor of water; is inflamed with difficulty, and burns with a sooty flame.

By the action of *nitric acid* upon *naphthalin*, the same products arise as by the action of that acid upon benzin; we obtain  $(C_8H_2, \curvearrowright C_{12}H_5)NO_4$  and  $(C_8H_2, \curvearrowright C_{12}H_3)3NO_4$ . By the union of both we obtain  $(C_8H_2, C_{12}H_4)2NO_4$ . By farther decomposition these com-

pounds are converted into phthalinic and nitrophthalinic acid. *Chlorine* and *bromine* behave in the same manner. *Concentrated sulphuric acid* gives with naphthalin sulphonaphthalid and sulphonaphthalid-sulphuric acid.

*Oxide of Naphthalid*:  $\text{NaO} = (\text{C}_8\text{H}_2, \text{C}_{12}\text{H}_5)\text{O} = \text{C}_{20}\text{H}_7\text{O}$ , is formed if nitronaphthalid be distilled with lime. A thick, yellow, oily fluid.

*Chloride of Naphthalid* (Chlornaphtase):  $\text{NaCl} = (\text{C}_8\text{H}_2, \text{C}_{12}\text{H}_5)\text{Cl} = \text{C}_{20}\text{H}_7\text{Cl}$ . This compound is obtained if hydrochlorate of chloride of naphthalid be several times distilled with potassa solution. Colorless, clear, oily fluid. If this compound be heated with *hydrate of sulphuric acid*, we obtain a paired acid, which consists of  $\text{HO}(\text{C}_8\text{H}_2, \text{C}_{12}\text{H}_5, \text{SO}_2, \text{Cl})\text{SO}_3$ .

*Hydrochlorate of Chloride of Naphthalid*:  $\text{NaCl} + \text{HCl} = (\text{C}_8\text{H}_2, \text{C}_{12}\text{H}_5)\text{Cl} + \text{HCl} = \text{C}_{20}\text{H}_8\text{Cl}_2$ . If chlorine gas be conducted over naphthalin, until the latter be converted into an oily body, we obtain a mixture of hydrochlorate of chloride of naphthalid with farther products of the decomposition of naphtha. From the etheric solution of this mixture, crystals are deposited, at  $-18^\circ$ , which consist of  $(\text{C}_8\text{H}_2, \text{C}_{12}\text{H}_5)\text{Cl}, \text{HCl} + \text{C}_8\text{H}_2(\text{C}_2\text{H}_2, \text{C}_6, \text{C}_2\text{H})\text{Cl}_3, 3\text{HCl} = \text{C}_{20}\text{H}_8\text{Cl}_4$ ; if the etheric solution, separated from the crystals, be left to spontaneous evaporation, at first naphthalin is separated, and later the hydrochlorate of chloride of naphthalid. Yellowish, oil-like, heavy fluid; insoluble in water, easily soluble in alcohol and ether; decomposes by dry distillation into hydrochloric acid, and  $\text{C}_{20}\text{H}_6\text{Cl}_2 = (\text{C}_{20}\text{H}_7)\text{Cl} + (\text{C}_{20}\text{H}_5)\text{Cl}_3$ . By action of nitric acid different products arise, as  $\text{C}_{20}\text{H}_5\text{Cl}_2\text{O}_3, \text{C}_{20}\text{H}_4\text{ClO}_5, \text{C}_9\text{H}_4\text{Cl}_3\text{O}$ , and nitrophthalinic acid  $(\text{C}_{16}\text{H}_3, \text{NO}_4)\text{O}_6$ .

*Hydrobromate of Bromide of Naphthalid*:  $\text{NaBr} + \text{HBr} = \text{C}_{20}\text{H}_8\text{Br}_2$ , is obtained by the action of bromine upon naphthalin. Crystallizes from the alcoholic solution in colorless, long six-sided prisms; inodorous, insoluble in water, easily soluble in alcohol and ether. Chlorine expels the bromine. Gives with hydrated sulphuric acid a paired sulphur acid  $(\text{C}_{20}\text{H}_6, \text{SO}_2)\text{SO}_3$ .

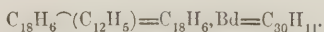
*Nitronaphthalid*:  $\text{NaNO}_4 = \text{C}_{20}\text{H}_7\text{NO}_4$ . Naphthalin is boiled with nitric acid, until an oily substance separates upon the surface, which stiffens crystalline by cooling. By recrystallization from the alcoholic solution nitronaphthalid is obtained in sulphur-yellow, four-sided prisms, which melt at  $43^\circ$ ; do not dissolve in water, but dissolve easily in alcohol and ether. If hydrosulphuric acid be conducted into the alcoholic solution, we obtain a base naphthalidin:  $\text{NH}_2\text{C}_{20}\text{H}_7$ . With *concentrated sulphuric acid* arises a paired sulphur acid  $\text{HO}(\text{C}_{20}\text{H}_6, \text{SO}_2)\text{NO}_4, \text{SO}_3$ , which is also procured by the action of nitric acid upon sulphonaphthalin-sulphuric acid. If nitronaphthalid be distilled with 8 parts of *lime*, an oily, yellow liquid goes over, which consists of  $\text{C}_{20}\text{H}_7\text{O}$  (*vide* above, Oxide of Naphthalid).

*Sulphonaphthalid* (Sulphonaphthalin):  $\text{Na}_2\text{SO}_2 = (\text{C}_8\text{H}_2, \text{C}_{12}\text{H}_5)\text{SO}_2$

$\text{SO}_2 = \text{C}_{20}\text{H}_7 + \text{SO}_2$ . To fuming sulphuric acid naphthalin is added little by little to saturation. The mass diluted with water and the precipitate which forms, is distilled with water, until all the naphthalin is gone over with aqueous vapor. The residue is treated with cold alcohol, which dissolves the sulphonaphthalid and leaves behind another body of the same constitution. From the alcoholic solution sulphonaphthalid is obtained in white, leafy warts, tasteless and inodorous, which fuse at  $70^\circ$  to a transparent yellow liquid; after cooling, we obtain a hard, yellowish mass similar to resin, which, by rubbing, becomes strongly electric; and insoluble in water, soluble in alcohol with difficulty, and rather easily in ether.

*Sulphonaphthalid-sulphuric Acid:*  $\text{HO}(\text{Na}, \text{SO}_2)\text{SO}_3$ . In completely pure hydrate of sulphuric acid, heated to  $70^\circ$ , naphthalin is dissolved till saturation; a thick liquid is produced, which, after a few days, stiffens in the air. Free sulphuric acid is removed from the mass, by pressing between filter paper; there remains a mixture of sulphonaphthalid-sulphuric acid with the so-called bisulphonaphthalid-sulphuric acid. This is dissolved in water, the solution saturated with baryta, filtered, and the filtrate evaporated as far as possible; afterward a double volume of alcohol is added, by which the bisulphonaphthalid-sulphate of baryta is precipitated. By evaporation of the alcoholic solution, we obtain the sulphonaphthalid-sulphate of baryta, from which the acid is obtained in the usual way. It appears as a colorless, inodorous, and brittle mass of sour and bitter taste; deliquesces in the air, dissolves in all proportions in water, and is farther soluble in alcohol, olive oil, and oil of turpentine. The acid, dried in a vacuum, contains 2 atoms water. If the acid be treated with nitric acid, we obtain nitro-sulphonaphthalinic acid. With *bases* it gives salts soluble in water, and mostly so in alcohol, tasting bitter, and burning with sooty flame; these, like the pure acid, decompose in the heat accompanied by evolution of sulphurous and carbonic acid gas, and there remains a mixture of sulphur-metal and carbon.

#### 4. ANTIIRACID:



*Hydroanthracid* (Anthracin, Paranaphthalin):  $\text{C}_{18}\text{H}_6$ , Hydroanthracid.  
 $\curvearrowright (\text{C}_{12}\text{H}_5)\text{H} = \text{C}_{30}\text{H}_{12}$ , is found in coal tar; the method of production was given in connection with naphthalin. It is obtained pure by repeated distillation. It agrees in properties with naphthalin, but does not fuse below  $300^\circ$ ; completely sublimable; insoluble in water, scarcely soluble in alcohol and ether, easily soluble in oil of turpentine. If we let anthracin boil a few minutes with nitric acid, it is converted into a yellow mass accompanied by evolution of nitrous acid; the mass stiffens after cooling. If this mass be washed with water, and then treated with ether, a



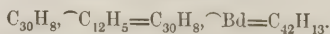
body remains behind, which consists of  $C_{30}H_9NO_6 = (C_{30}H_9)O, NO_5$ . This body melts at a high temperature, and by cooling stiffens to a mass consisting of long needles. If the etheric solution be evaporated and the residue treated with quite pure ether, there remains *binitro-anthracid*  $= C_{30}H_{10}, 2NO_4 = (C_{30}H_{11})NO_4 + (C_{30}H_9)3NO_4$ ; the same separates from the boiling etheric solution as a yellow, inodorous powder scarcely crystalline; insoluble in water, hardly soluble in boiling alcohol, and easily soluble in boiling ether. In the etheric solution poured off from the binitroanthracid, a compound remains, which consists of  $C_{30}H_{12}O_3 + 3NO_4$ ; it appears as an orange-red, resinous mass, easily fusible and readily soluble in ether. If hydroanthracid be a long time boiled with *nitric acid*, at last complete solution takes place, and after cooling colorless needles separate, which consist of  $HO, (C_{30}H_8NO_4), O_3 = (C_{18}H_3, \frown C_{12}H_5, \frown NO_4)O_3$ . This compound is pale-yellow, insoluble in water, easily soluble in alcohol and ether; melts, and by cooling stiffens in needles.

The product obtained by the action of *chlorine* upon anthracin crystallizes from the etheric solution in yellow leaflets, and consists of  $C_{30}H_{10}Cl_2 = C_{30}H_{11}Cl + C_{30}H_9Cl_3$ .

*Pyren*:  $C_{30}H_{12}$ , is isomeric with anthracin, and is

found in tar from wood, coal, and oil. If the last be distilled until one-fourth remains, and the residue be again submitted to distillation in a small retort, until carbon only remains behind, there appears in the neck of the retort a reddish substance, which consists of pyren, *hydrochrysid*, and empyreumatic oils; if this mixture be treated with ether, the hydrochrysid remains behind, and if the etheric solution be slowly evaporated, the pyren is then precipitated. Crystallizes from the boiling alcoholic solution in clear rhombohedral prisms, resembling tallow powder; melts at 170 to 180°, and stiffens crystalline; inodorous, tasteless; insoluble in water, little soluble in ether and alcohol; on the contrary, easily soluble in oil of turpentine. Boiled with nitric acid gives a combination, which consists of  $C_{30}H_{10}, 2NO_4$ .

## 5. CHRYSID:



*Hydrochrysid*. *Hydrochrysid* (Chrysen):  $(C_{30}H_8, C_{12}H_5)H$ . The production of hydrochrysid was given in connection with pyren; appears as a yellow, inodorous, and tasteless powder; insoluble in water and alcohol, and scarcely soluble in ether and oil of turpentine; fuses at 230 to 235°; stiffens crystalline. If it be boiled with nitric acid until it is completely dissolved, we obtain a compound, which is said to consist of  $C_{24}H_6N_2O_5$ .

*Idryl*:  $C_{42}H_{14}$ . This body, isomeric with hydrochrysid, is pro-

cured from the so-called *stupp* (dross), which is obtained in the form of a black mass by distillation of the bituminous mercury ore employed in Idria for procuring mercury. If this substance be completely extracted by boiling with alcohol, during the cooling of the solution there separate yellow leaflets. If, after the deposition of the leaflets, the alcoholic solution be submitted to distillation, an oily brown-black mass separates, and if this be treated with boiling acetic acid, idryl crystallizes from the acetic acid solution after cooling in rhombic microscopic leaflets; colorless, fuses at  $86^{\circ}$ , and stiffens to a radiated, almost colorless mass; sublimable; little soluble in cold alcohol, ether, acetic acid, and oil of turpentine, but easily soluble in the heat. *Concentrated sulphuric acid* dissolves it at  $100^{\circ}$ , with deep greenish-yellow color.

*Idrialin*:  $C_{42}H_{14}O$ , is found in burnt ore of mercury of Idria, and sublimes, if the pulverized ore be heated in a stream of carbonic acid. Crystallizes in small woolly scales; fusible with difficulty; volatile; insoluble in water, and soluble with difficulty in boiling alcohol and ether. Appendix to  
naphthalin and  
anthracin.  
Idrialin.

*Retisterin*:  $(C_{20}H_{38}, ^-C_{12}H_5)H$ , is found in rosin-tar. It consists of several compounds, which can be separated by fractional distillation; at  $130$  to  $160^{\circ}$  *tolin* generally goes over; at  $260$  to  $280^{\circ}$  *retinyl*, at  $280$  to  $300^{\circ}$  *retinol*, and at  $350^{\circ}$  retisteren as a fat-like matter. It is in pure state white, crystalline, unctuous, without taste or smell; melts at  $67^{\circ}$ ; insoluble in water, little soluble in cold alcohol and ether, but easily soluble in boiling. Nitric acid and chlorine decompose the compound. Retisterin.

By compression of the resin gases a liquid is obtained, which, by fractional distillation, can be separated into several fluid compounds consisting of  $C_{16}H_{16}$ ,  $C_{20}H_{16}$ ,  $C_{24}H_{16}$ ,  $C_{28}H_{16}$ ,  $C_{32}H_{16}$ .

*Retinol*:  $C_{32}H_{16}$ , occurs, as was just observed, in resin-tar; clear fluid, without taste or smell; boils at  $238^{\circ}$ . Retinol.

*Eupion* is the name of a substance obtained by the distillation of fatty oils, especially rape-seed oil; a colorless, tasteless, indifferent, fatty fluid, which may combine directly with chlorine and bromine; what this substance is, we know not. Eupion.

Several species of bituminous strata give by distillation an oily product. If this be treated with concentrated sulphuric acid, and then several times rectified over caustic potassa and anhydrous phosphoric acid, we obtain, by fractional distillation, combinations which consist of  $C_{36}H_{16}$  (at  $132$  to  $135^{\circ}$ );  $C_{52}H_{24}$  (at  $215$  to  $220^{\circ}$ );  $C_{56}H_{26}$  (at  $255$  to  $260^{\circ}$ );  $C_{72}H_{34}$  (at  $275$  to  $280^{\circ}$ ). These bodies all give, with nitric acid, nitro-compounds, and the latter, treated with sulphide of ammonium, organic bases. If the oil, which

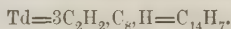
Ampelinic  
acid.

distils over at  $150^{\circ}$ , be boiled with nitric acid, we obtain an acid which is named *ampelinic acid*, and which probably is allied to phthalinic acid.

Yet to be mentioned are the names: *Fichtelite*,  $C_{24}H_{18}$ , which is found in a turf-bed in Fichtel Mountain. *Hartite*,  $C_{24}H_{20}$ , found in Hart brown coals. *Retinite*,  $C_{24}H_{18}O_2$ , occurs in the coal-mines of Walchow, in Mähren. *Tekoretin* and *Phylloretin*,  $C_{24}H_{20}$ , are found in fossil pine-trees, and in the swamps of Holtegaard. *Scheererite* is sometimes found in brown coal-beds near Utznach, on Lake Zurich. *Succisterin* is said to be obtained by dry distillation of amber, etc.

### THIRD MEMBER.

#### TOLID:



Hydrotolid.

*Hydrotolid* (Tolin, Benzoën, Toluol, Dracyl, Retinaphtha):  $TdH$ , is obtained, if toluylic acid  $HO(3C_2H_2, C_8, C_2H)O_3$ , be distilled with an excess of baryta; is found in coal tar (*vide* Hydrobenzid): arises by dry distillation of ordinary resins (*vide* Retisterin), the tolu-resins, dragon's blood, etc. Colorless, very mobile fluid, insoluble in water, soluble with difficulty in alcohol, and easily soluble in ether; of etheric odor, like that of hydrobenzid, and burning taste; sp. gr. 0.864; boils at  $109^{\circ}$ . To *nitric acid*, *chlorine*, *bromine*, and *sulphuric acid*, tolin behaves in general like hydrobenzid.

*Chloride of Tolid*:  $TdCl = C_{14}H_7Cl$ , is obtained, if hydrotolid be exposed 8 days in a dark room to the action of chlorine gas, and the obtained fluid distilled until hydrochloric acid is evolved. The distillate is again rectified. A colorless, very mobile fluid, which boils at  $170^{\circ}$ , and volatilizes without decomposition. Is converted by farther action of chlorine first into hydrochlorate of chloride of benzoyl  $(C_{14}H_5)Cl_3 + HCl$ , then into hydrochlorate of chlororide of bichlorobenzoyl  $(C_{14}H_3Cl_2)Cl_3 + 2HCl$ , and at last into  $C_{14}H_2Cl_6$ .

*Nitrotolid*:  $Td, NO_4 = C_{14}H_7, NO_4$ . Hydrotolid is dissolved in the cold in fuming nitric acid, and the red solution immediately mixed with a large quantity of water, by which the nitrotolid with red color is precipitated. It is repeatedly washed with water, and obtained in pure condition by repeated distillation with water. Forms a water-clear fluid, of sugar-sweet taste, smelling like oil of bitter almonds; insoluble in water, but easily soluble in alcohol and ether; of 1.18 sp. gr. If nitrotolid be conducted over glowing lime, it decomposes into anilin and carbonic acid. The alcoholic solution saturated with hydrosulphuric acid gives *toluidin*  $NH_2Td$ . Is converted by farther action of *nitric acid* into the so-called

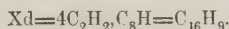
*binitrolid*, which consists of nitrotolid +  $(C_{14}H_5)3NO_4$ . By long boiling hydrotolid with nitric acid, we obtain nitrobenzoic acid (?) (nitrotolinic acid).

*Sulphotolid*:  $Td, SO_2(?)$ . If the solution of hydrotolid in fuming sulphuric acid be mixed with water, there is precipitated a shining crystalline body, sulphotolid; and in the solution is found

*Sulphotolid-sulphuric Acid*:  $HO(Td, SO_2, \frown SO_3)$ , which is obtained in the ordinary manner. If the aqueous solution of the acid be first evaporated upon the water bath, and then in a vacuum, it crystallizes in white leaves, which soon become moist in the air. It decomposes at a high temperature, under evolution of sulphurous acid, and gives with bases salts easily soluble.

## FOURTH MEMBER.

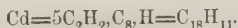
## XYLOID:



The hydrogen compound of Xyloid, Xyloidin, is found in tar. Yet not particularly known.

## FIFTH MEMBER.

## CUMID:



*Hydrocumid* (Cumin, Cumyl):  $CdH$ . It is obtained from cuminic acid in the same manner as hydrobenzid from benzoic acid, and hydrotolid from toluyllic acid. Is also found in coal tar (*vide* Benzid). Colorless fluid, smelling agreeably, like hydrobenzid; strongly refracts light; insoluble in water, but easily soluble in ether, alcohol, and wood-spirit; of 0.887 sp. gr.; boiling point  $144^\circ$ . Gives with *fuming nitric acid* nitrocumid,  $Cd, NO_4 = C_{18}H_{11}, NO_4$ , and *binitrocumid* =  $Cd, NO_4 + (4C_2H_2, C_8, C_2H)3NO_4$ ; immediately it forms nitrobenzoic acid, and by longer action of dilute nitric acid, benzoic acid. Forms with fuming sulphuric acid *sulphocumid-sulphuric acid*,  $HO(Cd, SO_2) \frown SO_3$ , whose baryta salt crystallizes in beautiful leaflets, of mother-of-pearl lustre; soluble in water, alcohol, and ether.

*Retinyl*:  $C_{18}H_{12}$ . This compound is found in crude resin oil, by the fractional distillation of which it goes over at  $150^\circ$ . Is decomposed by nitric acid and chlorine; gives with sulphuric acid the sulphoretinyl-sulphuric acid, whose baryta salt is soluble in alcohol with greater difficulty than that of the corresponding sulphocumid-sulphuric acid.

*Mesitol* (Mesitylen):  $C_{13}H_{12}$ . This body is obtained when acetone is distilled by a gentle heat with half its volume of sulphuric acid. The distillate consists of an aqueous

Hydrocumid.

Compounds  
isomeric with  
hydrocumid.  
Retinyl.

Mesitol.



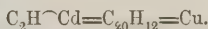
fluid containing sulphurous acid; upon the surface of this fluid, the mesitol swims, and is purified by rectification; at  $155^{\circ}$  the pure compound goes over; a light colorless fluid, of feeble garlic odor; boils at  $155$  to  $160^{\circ}$ .

If mesitol be treated some time with *fuming nitric acid*, we obtain *trinitro-mesitol*  $(C_{18}H_9)3NO_4$ ; by using dilute acid, a combination arises of  $(C_{18}H_{11})NO_4 + (C_{18}H_9)3NO_4$ , or the so-named *binitro-mesitol*. The former compound is fluid, and possesses a sweet penetrating smell and taste; the latter crystallizes in fine needles; both give, when treated with hydrosulphuric acid, organic bases, *nitro-mesidin* and *binitro-mesidin*.

Simultaneously with the above-mentioned bodies is formed a thick, heavy, reddish fluid, of sweet penetrating odor, which must consist of  $C_{18}H_{12}O_6$ . By the action of *chlorine* and *bromine* upon mesitol, we obtain  $(C_{18}H_9)Cl_3$  and  $(C_{18}H_9)Br_3$ . The *chlorine compound* crystallizes in colorless, quadrilateral prisms, which are insoluble in water, and not changed by potassa. Also a corresponding *iodine compound* is said to exist in the form of golden-yellow powder, which crystallizes from the etheric solution in spangles. *Fuming sulphuric acid* dissolves mesitol to a brown fluid, under formation of mesito-sulphuric acid  $HO(C_{18}H_{11}SO_2)^-SO_3$ .

#### PAIRED RADICAL OF CUMID.

##### CUMYL:



Cuminol.

*Cumyl* behaves to cumid as picramyl to benzid.

*Oxide of Cumyl* (Cuminol):  $CuO_2$ , occurs in common with hydrocymid in Roman cumin oil. If this is distilled in an oil-bath, the hydrocymid goes over at  $165^{\circ}$ , and in the residue the cumin oil remains as a colorless fluid, retaining a strong odor of Roman cumin oil, and a sharp burning taste; boils at  $220^{\circ}$  (bitter almond oil at  $176^{\circ}$ ). By the action of *cyanide of potassium*, cumin oil is converted into a product resembling benzoin. In the air, and by influence of oxidation, we obtain from cumin oil cuminic acid  $HO(5C_2H_2, C_8, C_2H)O_3$ . If we boil cumin oil a long time with *nitric acid*, we obtain nitro-cuminic acid. *Chlorine* and *bromine* give with cumin oil *bioxychloride*, or *bioxybromide of cuminyll*  $= (5C_2H_2, C_8, C_2H) \left\{ \begin{matrix} O \\ Cl \end{matrix} \right\}_2$ , and  $(5C_2H_2, C_8, C_2H) \left\{ \begin{matrix} O \\ Br \end{matrix} \right\}_2$ . If a piece of *dry hydrate of potassa* be brought into cumin oil, we obtain a gelatinous mass, which decomposes into cumin oil and potassa, by solution in water. Melted with *hydrate of potassa*, cuminic acid arises with evolution of hydrogen gas.

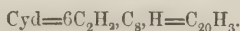
*Chloride of Cumyl*:  $CuCl_2$  is obtained, if chloride of phosphorus

with cumin oil be submitted to distillation. A fluid, boiling at 255 to 260°; insoluble in water, easily soluble in alcohol and ether. If the alcoholic solution be mixed with an alcoholic solution of KS, HS, a disagreeably smelling body is formed, probably sulphide of cumyl,  $\text{CuS}_2$ .

Isomeric with cumin oil is *parinicen*, which has already been mentioned at protochloride of nicid (page 193).

## SIXTH MEMBER.

## CYMID:



*Hydrocymid* (Cymin, Cumen):  $\text{Cy dH}$ , is found in *Hydrocymid*. Roman cumin oil (*vide* Oxide of Cumyl). The first portion, which goes over in the distillation of this oil is rectified over hydrate of potassa, whereby the yet present cumin oil is converted into cuminic acid. If we lead moist carbonic acid together with oil of turpentine through a tube heated to dull-redness, we obtain a very mobile fluid of the same constitution as hydrocymid; also by the distillation of camphor with anhydrous phosphoric acid, the same compound seems to be formed (*camphon*). A colorless fluid, powerfully refracting light, of pleasant lemon-like odor; insoluble in water, easily soluble in alcohol and ether; sp. gr. 0.856; boiling point 171.°5.

If we distil hydrocymid with very *dilute nitric acid* two or three days (whilst we continually pour back the distillate into the retort), or, until in the condensed water in the receiver no more drops of oil are separated, but a white crystalline mass appears, thus, after cooling, the retort is filled with crystals of *toluylic acid*  $\text{HO}(\text{C}_{16}\text{H}_7)\text{O}_3$ . If we treat hydrocymid with *fuming nitric acid*, we obtain nitro-toluylic acid. Chromic acid as well as peroxide of manganese and sulphuric acid do not act upon hydrocymid.

Hydrocymid with *concentrated sulphuric acid* forms sulphocymid-sulphuric acid  $\text{HO}(\text{Cy}, \text{SO}_2)\text{SO}_3$ , which appears in small crystals.

*Tolen*:  $(8\text{C}_2\text{H}_2, \text{C}_8, \text{H})\text{H} = \text{C}_{24}\text{H}_{18}(?)$ . This body is <sup>Tolen.</sup> said to occur in tolu balsam, and to be obtained by distillation of that substance with water; it boils at 170°.

## BENZOYL GROUP.

Component  $\text{C}_2\text{H}_2$ ; Nucleus  $\text{C}_8$ ; Active part  $\text{C}_2\text{H}$ .

The radicals of the benzoyl group behave to those of the benzid group like the radicals of the formyl group to those of the methyl group.

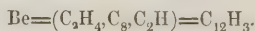
They now include the following members:—

Member 1.	Benzyl,	$\text{Be} = \text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H} = \text{C}_{12}\text{H}_3.$
“ 2.	Benzoyl,	$\text{Bz} = 2\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H} = \text{C}_{14}\text{H}_5.$
“ 3.	Toluyll,	$\text{To} = 3\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H} = \text{C}_{16}\text{H}_7.$
“ 4.	Unknown, (?)	$= 4\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H} = \text{C}_{18}\text{H}_9.$
“ 5.	Cuminyll,	$\text{Cy} = 5\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H} = \text{C}_{20}\text{H}_{11}.$

The radicals of this group, like those of the formyl group, combine with three atoms of oxygen to form acids which are remarkable for their durability; and several give also with the halogens and  $\text{NO}_4$  corresponding compounds. They are formed when the corresponding members of the benzid group have absorbed two atoms of hydrogen. Thus is benzid  $\text{C}_{12}\text{H}_5 - 2\text{H} = \text{Benzyl}$ , likewise tolid  $\text{C}_{14}\text{H}_7 - 2\text{H} = \text{Benzoyl}$ , etc. All the acids of this group are solid, possess the capability of crystallization, are sublimable, slightly soluble in cold water, more easily in hot, and easily soluble in alcohol, and give with alkalies durable salts, very soluble in water; and hence, if we add to concentrated salt solutions a stronger acid, a greater part of the acids is precipitated, and upon this fact is based the method of their production. In the pure state they are tasteless and inodorous; melt like oil, and stiffen crystalline. By dry distillation of their neutral alkali salts, we obtain paired radicals, which correspond to those of the acetonyl group. Thus from benzoic acid arises benzon  $= (\text{C}_{12}\text{H}_5, \text{C}_{14}\text{H}_5)\text{O}_2 = \text{Bd}, \text{BzO}_2$ , corresponding to acetone  $(\text{C}_2\text{H}_3, \text{C}_4\text{H}_3)\text{O}_2$ . If the hydrates are distilled with an excess of hydrate of potassa, we obtain the corresponding hydrogen compounds of the benzid group; thus the hydrate of benzoic acid  $\text{HO}(2\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H})\text{O}_3$  gives benzid  $(2\text{C}_2\text{H}_2, \text{C}_8, \text{H})\text{H} + 2\text{CO}_2$ . By the action of the halogens and of nitric acid, we obtain derived compounds. The radicals of this group correspond in gaseous state to two volumes; they are as yet unknown in an isolated state.

#### FIRST MEMBER.

#### BENZYL:



This radical is formed from benzid, if the latter absorbs 2 atoms hydrogen; hitherto only compounds with the halogens and  $\text{NO}_4$  are known.

*Chloride of Benzyl* (Chlorbenzid):  $\text{BeCl}_3 = \text{C}_{12}\text{H}_3$   
 Chlorbenzid.  $\text{Cl}_3$ , is formed, in common with hydrochlorate of chloride of benzid, by direct action of chlorine upon hydrobenzid (Benzin). If the latter compound be distilled with an excess of hydrate of lime, the chloride of benzyl passes over as an oily, colorless fluid, of 1.475 sp. gr. Insoluble in water, easily soluble

in alcohol, ether, and hydrobenzid; boils at  $210^{\circ}$ ; is not attacked by alkalis.

*Bromine*, exposed with hydrobenzid to the action of sunlight, gives corresponding compounds.

*Hydrochlorate of Chloride of Benzyl* (Chlorbenzin) Chlorbenzin.  
 $\text{BeCl}_3 + 3\text{HCl} = \text{C}_{12}\text{H}_6\text{Cl}_6$ . Into a large glass containing hydrobenzid, and upon which the sun shines, chlorine gas is conducted. After a little time, chloride of benzil is deposited in crystals; and if the operation be long continued, nearly all the hydrobenzid is converted into the compound. It separates from the saturated etheric solution in crystals; insoluble in water, not easily soluble in alcohol, easily soluble in ether; melts at  $132^{\circ}$ . Decomposes by distillation into hydrochloric acid and chloride of benzyl.

*Benzylnitrid* (Trinitrobenzin):  $\text{Be}, 3\text{NO}_4 = (\text{C}_{12}\text{H}_3)$  Binitrobenzid.  
 $3\text{NO}_4$ , is only known in combination with nitrobenzid as the so-called *binitrobenzid*  $= (\text{C}_{12}\text{H}_5)\text{NO}_4 + (\text{C}_{12}\text{H}_3)3\text{NO}_4 = \text{C}_{12}\text{H}_4, 2\text{NO}_4$ . If hydrobenzid (benzin) be brought by drops into a mixture of equal parts of fuming sulphuric and fuming nitric acid, so long as the two fluids mingle, and the mixture then heated a few minutes, the whole mass stiffens in cooling to a thick crystal paste of binitrobenzid, which being mixed with water, and repeatedly crystallized from the alcoholic solution, is obtained in long, shining, crystal needles. If the alcoholic solution be treated with sulphide of ammonium, we obtain nitranilin,  $\text{NH}_2(\text{C}_{12}\text{H}_4, \text{NO}_4)$  under deposition of sulphur.

#### PAIRED COMBINATIONS OF BENZYL.

*Chloride of Naphtyl* (Trichlornaphthalin):  $\text{C}_8\text{H}_2, \text{C}_8\text{H}_2, \text{C}_8\text{H}_2\text{Cl}_3 = \text{C}_{20}\text{H}_5\text{Cl}_3$ . This compound is obtained when chlorine acts upon hydronaphthalid (naphthalin) in the heat, and by co-operation of direct sunlight. Crystallizes in inodorous prisms, an inch long; melts at  $75^{\circ}$ , and may be distilled at  $200^{\circ}$ ; insoluble in water, almost insoluble in alcohol, easily soluble in ether. Gives with sulphuric acid a paired acid  $= \text{HO}(\text{C}_8\text{H}_2, \text{C}_2\text{H}_2, \text{C}_8, \text{C}_2, \text{SO}_2) \text{SO}_3$ . Naphtyl compounds. Trichlor-naphthalin.

*Chloride of Naphtyl-naphthalid* (Naphtylchlorid-chlornaphthalid):  $\text{C}_8\text{H}_2, (2\text{C}_2\text{H}_2, \text{C}_8, \text{H}_2)\text{Cl} + \text{C}_8\text{H}_2, (\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H}_2)\text{Cl}_3 = \text{C}_{20}\text{H}_6\text{Cl}_2$ , or the so-called bichlor-naphthalid, is obtained, if the following compound is distilled with hydrate of potassa. Crystallizes from the alcoholic solution in transparent, long, slender prisms; tasteless and inodorous; insoluble in water, easily soluble in alcohol and ether; melts at  $44^{\circ}$ ; gives with sulphuric acid a paired acid  $= \text{HO}(\text{C}_{20}\text{H}_5, \text{SO}_2, \text{Cl}_2) \text{SO}_3$ . Bichlornaphthalid.

*Hydrochlorate of Proto- and Ter-chloride of Naphthalid* (Salz-



saures Naphthalidechlorid-naphthalidechlorur):  $C_8H_2, \wedge (2C_2H_2, C_8, H) Cl, HCl + C_8H_2, \wedge (C_2H_2, C_8, C_2H) Cl_3, 3HCl = C_{20}H_8Cl_4$ ) or, the so-called fourfold chlornaphthalin is obtained, if *hydrochlorate of chlornaphthalin* (chloride of hydronaphthalid) comes in contact with chlorine in the cold. Crystallizes from the etheric solution in transparent rhombic tables; possesses a strong odor; melts at  $160^\circ$ ; insoluble in water, soluble with difficulty in alcohol and ether; sublimes in an open vessel, without decomposition. If it be distilled with hydrate of potassa, proto- and terchloride of naphthalid goes over. *Nitric acid* decomposes the compound under production of oxalic, phtalinic, and nitro-phtalinic acid.

*Terchloride of Naphtyl-bichlornaphtyl* (Bichlornaphtylechlorid-naphtylechlorid, Tetrachlornaphthalin):  $= C_8H_2, \wedge (C_2H_2, C_8, C_2H) Cl_3 + C_8H_2, \wedge (C_2Cl_2, C_8, C_2H) Cl_3 = C_{20}H_4Cl_4$ , is obtained by the action of chlorine upon chloride of naphtyl in boiling heat. Crystallizes in hexagonal needles; easily soluble in alcohol and ether; melts at  $126^\circ$ ; sublimable, and gives, with hydrate of sulphuric acid, a paired acid  $= HO(C_{20}H_3, SO_2, Cl_4) \wedge SO_3$ .

*Naphtylnitrid* (Trinitronaphthalid):  $C_8H_2, \wedge (C_2H_2, C_8, C_2H) 3NO_4 = C_{20}H_5, 3NO_4$ , is formed by the action of nitric acid upon nitronaphthalid in common with the following combination. Crystallizes in rhombic tables of pale-yellow color; inodorous; insoluble in water, sparingly soluble in alcohol and ether; melts at  $200^\circ$ ; decomposes in contact with an alcoholic solution of potassa into carbonic, formic, hydrocyanic and nitronaphthalinic acid  $C_{20}H_6N_2O_{10} = (C_{24}H_6) 2NO_5 (?)$ .

*Naphtylnitrid-nitronaphthalid* (Binironaphthalid):  $C_8H_2, \wedge (2C_2H_2, C_8, H) NO_4 + C_8H_2, \wedge (C_2H_2, C_8, C_2H) 3NO_4 = C_{20}H_6 2NO_4$ . Crystalline, neutral powder; insoluble in water, soluble with difficulty in alcohol and ether; melts at  $175^\circ$ ; sublimes unchanged; gives, with sulphide of ammonium, a base nitronaphthalidin, and, brought together with an alcoholic potassa solution, decomposes into ammonia, carbonic acid, and a new acid, which consists of  $C_{32}H_9N_9O_8$ .

*Naphtylsulpho-sulphuric Acid*:  $3HO(C_8H_2, C_2H_2, C_8, C_2H, 3SO_2) \wedge 3SO_3 = 3HO(C_{20}H_5, 3SO_2) \wedge 3SO_3$ , forms with sulphonaphthalid-sulphuric acid the *bisulphonaphthalin-sulphuric acid* (naphthalin-hypo-sulphuric acid)  $= HO(C_{20}H_7, SO_2) SO_3 + 3HO(C_{20}H_5, 3SO_2) 3SO_3 = 2HO_2(C_{20}H_6, 2SO_2) 2SO_3$ . For production of this acid, see Sulphonaphthalid-sulphuric acid.

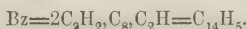
Talcose powder is colored in the air, especially in moist state in the sunlight; tastes acid and bitter, remains dry in the air; easily soluble in alcohol and ether. Its salts bear a high temperature; they taste bitter; the acid saturates 2 atoms of base.

By the action of sulphuric acid upon naphthalin, yet a third acid arises, which is named *glutinhyposulphuric acid*; it does not crystallize, but dries to a hard colorless mass, of bitter and sour taste, easily soluble in water and alcohol. Glutin-hypo-sulphuric acid.

Here also belong the paired acids, which are formed by the action of sulphuric acid upon chloride of naphthyl, *naphthylchlorid-chlornaphthalid*, etc., and have been already mentioned above; likewise the sulphonitronaphthalin-sulphuric acid, etc.

## SECOND MEMBER.

## BENZOYL:



*Benzoyl* is found in combination with oxygen as benzoic acid in benzoin balsam. It arises from picramyl and its paired combinations, as cinnamon oil, and cinnamein; farther, by the oxidation of the higher members of the radicals of the benzid group, etc. With oxygen two combinations are known.

*Oxide of Benzoyl*:  $\text{BzO}_2$ . If benzoate of copper be heated in a retort, drops collect in the receiver, which stiffen to a crystalline mass, and consist of Oxide of benzoyl. the oxide of benzoyl and benzoic acid, and as a residue the sali-cylate of protoxide of copper remains. The benzoic acid of the mixture is absorbed by carbonate of soda, and the oxide of benzoyl remaining behind, is obtained by repeated crystallization from the hot alcoholic or etheric solution in large four-sided, oblique, hard and brittle prisms. It fuses at  $70^\circ$ ; possesses an agreeable lemon-like odor; if it be heated a long time with a potassa solution under access of air, we obtain benzoate of potassa. Nitric acid oxidizes it instantaneously, forming benzoic acid. If oxide of benzoyl be exposed several days in a melted state to the action of chlorine, it forms a compound, which is obtained from the etheric solution in large aromatic crystals; they consist of  $\text{C}_{28}\text{H}_9\text{ClO}_4$ .

*Hydrate of Benzoic Acid* (Benzoic Acid):  $\text{HOBz}$  Benzoic acid.  
 $\text{O}_3$ . Benzoic acid is obtained from benzoin resin, by careful sublimation in gentle heat. It is generally formed by dissolving the resin in an equal volume of alcohol, saturating the solution with carbonate of soda, then mixing with water, and distilling away the alcohol. From the aqueous solution removed from the residue, the benzoic acid is precipitated by hydrochloric acid. It crystallizes from the hot saturated aqueous solution in the form of a rhombic prism; in pure state inodorous, the taste is warming, sharp, somewhat sour, and long continued; melts at  $120^\circ$ , like a fat, stiffens crystalline, boils at  $239^\circ$ , and forms vapor,

which excites tears and violent coughing. Benzoic acid dissolves in 200 parts cold water, and 30 parts hot; it is easily dissolved in alcohol, ether, and fatty oils. If hydrate of benzoic acid be conducted through a *glowing tube*, or if it be subjected to dry distillation, with an excess of hydrate of lime, it decomposes into hydrobenzid ( $C_{12}H_5$ )II and  $2CO_2$ ; on the contrary, if neutral benzoate of lime be distilled, there arises benzon ( $C_{12}H_5 \curvearrowright C_{14}H_5$ )O<sub>2</sub>. If benzoic acid be treated a few hours with *fuming sulphuric* and *fuming nitric acid*, we obtain *binitrobenzoic acid*; if *nitric acid* alone be employed, a compound is formed of benzoic acid with binitrobenzoic acid. If we distil benzoic acid with *chloride of phosphorus*, thus arise bioxychloride of phosphorus, and also oxychloride of benzoyl  $(C_{14}H_5) \left\{ \begin{smallmatrix} O_2 \\ C. \end{smallmatrix} \right.$  Chlorine converts benzoic acid little by little into *bichlorbenzoic* and *tetrachlorbenzoic acid*; in the beginning, a compound is formed of benzoic with bichlorbenzoic acid, and by the union of the bichlor- with the tetrachlorbenzoic acid, the so-called trichlorbenzoic acid is formed. By the action of *anhydrous sulphuric acid* upon benzoic acid, we obtain the sulphobenzo-sulphuric acid =  $HO(C_{14}H_4SO_2) \curvearrowright SO_3$ . If chlorine gas be conducted into a strong alkali solution of benzoic acid, we obtain chlorniceinic acid (p. 193) under evolution of carbonic acid.

*Benzoic Acid Salts.* Benzoic acid forms neutral and basic salts, which mostly are soluble in water. They possess a peculiar warming taste. If in solutions not too dilute they are mixed with a mineral acid, the benzoic acid is mostly precipitated. With protoxide of iron benzoic acid forms a few insoluble basic salts. The insoluble salts are taken up in the heat by a solution of acetate of potassa or soda. The *ammonia salt* appears in penniform, easily soluble crystals, which by heating decompose into water and nitrobenzoyl. The *acid ammonia salt* is procured in granular crystals, if the neutral solution be rapidly evaporated. *Benzamid*  $NH_2, BzO_2$  is obtained, if ammonia gas be conducted over oxychloride of benzoyl; it separates from the hot aqueous solution by rapid cooling in pearly, crystal leaflets, and by slowly cooling we obtain a mass consisting of fine crystal needles, of silken lustre. In this mass, after a little time, cavities appear, in the middle point of which large perfect crystals are found; by degrees the whole changes into large crystals, of mother-of-pearl lustre, which behave to warm water like fat; fuse at  $115^\circ$ ; and at a high temperature distil unchanged. Benzamid is almost insoluble in cold water, but dissolves easily in alcohol and ether; it combines with 2 atoms bromine, and by treatment with acids and alkalies decomposes into benzoic acid and ammonia. *Bibenzamid*  $NH_2, 2BzO_2 = (NH, BzO) \curvearrowright BzO_3$ , is formed, if oil of bitter almonds remains a long time in contact with water. It appears as a white flaky mass, of mother-of pearl lustre, and consisting of fine needles, insoluble in

water, and easily soluble in alcohol and ether. Treated with an alcoholic solution of potassa, benzoic acid and ammonia are formed. It dissolves in fuming sulphuric acid, with an indigo-blue color. The *potassa salt*  $\text{KO}, \text{BzO}_3 + \text{aq}$ , forms fine penniform crystals. The *soda salt* appears in needles, which are soluble with difficulty in boiling alcohol. The *baryta salt* forms needles, not easily soluble in water. The *protoxide of manganese salt* requires 20 parts water for solution. The *neutral peroxide of iron salt*,  $\text{Fe}_2\text{O}_3, 3\text{BzO}_3$ , crystallizes in yellow needles, which are dissolved by alcohol and water, under separation of a basic salt. If a solution of perchloride of iron, mingled with ammonia, be mixed with benzoate of potassa, we obtain an insoluble compound, which consists of  $\text{Fe}_2\text{O}_3, 2\text{BzO}_3$ . The *silver salt* is deposited from the boiling solution in crystalline scales.

*Bioxy sulphide of Benzoyl*:  $\text{Bz} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{S} \end{smallmatrix} \right.$  distils over Bioxy sulphide of benzoyl.  
when bioxychloride of benzoyl is heated with finely pulverized sulphide of lead. Soft, crystalline, yellow mass, of disagreeable odor; forms with a concentrated solution of potassa, after some time, sulphide of potassium and benzoate of potassa.

*Chloride of Benzoyl*:  $\text{BzCl}_3 + \text{HCl}$ , is obtained, if chlorine be conducted into hydrotolid in the cold and under strong daylight, until it evolves no more hydrochloric acid gas. Colorless liquid, which cannot be distilled without evolution of hydrochloric acid. Chloride of benzoyl.

*Bioxychloride of Benzoyl*:  $\text{Bz} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right.$  is obtained, Bioxychloride of benzoyl.  
if dry chlorine gas be led into bitter almond oil, or if benzoic acid be distilled with chloride of phosphorus. Water-clear fluid of peculiar, highly penetrating odor, exciting the eyes to tears. Decomposes, in contact with water, into benzoic and hydrochloric acid; sp. gr. 1.190.

*Bioxybromide of Benzoyl*:  $\text{Bz} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Br} \end{smallmatrix} \right.$  a soft, large-leaved, crystalline mass of aromatic odor. Arises by the action of bromine upon oil of bitter almonds. Bioxybromide of benzoyl.

*Bioxyiodide of Benzoyl*:  $\text{Bz} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{I} \end{smallmatrix} \right.$  Goes over when Bioxyiodide of benzoyl.  
bioxychloride of benzoyl is distilled with iodide of potassium. Colorless, leafy, crystalline, easily fusible.

*Acetylchlorate of Bioxychloride of Benzoyl*:  $\text{Bz} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right. + \text{Ac} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right.$  (?), is obtained by the decomposition of benzoate of ethyl by chlorine. A colorless, slightly fuming fluid of 1.346 sp. gr. Decomposes in contact with water into benzoic, acetic, and hydrochloric acid.



*Benzoylnitrid*:  $Bz + 3NO_2$ , forms with nitrolid the so-named binitrolid. Is obtained, if tolin be a long time boiled with nitric acid. The crystalline precipitate, which forms, is purified by recrystallization. Appears in acicular, prismatic crystals of much lustre; melts at  $71^\circ$ , and stiffens to a radiated, hard, brittle mass. Is not decomposed by nitric acid, and by potash-lye dissolved with red-brown color.

*Nitrobenzoyl* (Benzonitryl):  $BzN$ , forms by heating benzoate of ammonia. Completely colorless fluid, of strong agreeable odor, like oil of bitter almonds; dissolves in 100 parts boiling water, and in every proportion in alcohol and ether; sp. gr. 1.0073; boils at  $191^\circ$ ; is converted by the co-operation of acids and alkalies into benzoic acid and ammonia. If the alcoholic solution be mixed with sulphide of ammonium, we obtain *benzoylsulphidamid*,  $NH_2, BzS_2$ , which crystallizes in long needles of satin lustre, and forms, when treated with oxide of mercury, nitrobenzoyl, and sulphide of mercury.

*Bichlorbenzoic Acid*:  $HO(C_2Cl_2, C_2H_2, C_8, C_2H)O_3 = HO, (C_{14}H_3Cl_2)O_3$ ; and *tetrachlorbenzoic acid*:  $HO(2C_2Cl_2, C_8, C_2H)O_3 = HO(C_{14}HCl_4)O_3$ : is formed by the action of chlorine upon benzoic acid: the decomposition takes place only slowly. In the beginning, we obtain a compound of benzoic with bichlorbenzoic acid, or the so-called *chlorbenzoic acid*, and by union of the bichlor- with the *tetrachlor-benzoic acid*, we obtain the *trichlorbenzoic acid*. These compounds are less soluble in water than benzoic acid; they dissolve easily in alcohol and ether, and by the spontaneous evaporation of their solutions crystallize in small stellated groups of silky needles. They combine with bases like benzoic acid.

*Hydrochlorate of Chloride of Bichlorbenzoyl*:  $= (C_2Cl_2, C_2H_2, C_8, C_2H)Cl_3 + 2HCl = C_{14}H_5Cl_7$ , appears a pasty, glutinous mass; it is formed simultaneously with the *hydrochlorate of superchloride of bichlorbenzoyl*  $(C_2Cl_2, C_2H_2, C_8, C_2H)Cl_5 + 3HCl$ , if chlorine act a long time in the sunlight upon tolin. Crystallizes and much resembles benzoic acid. By farther action of chlorine, we obtain a compound, which consists of  $C_{14}H_2Cl_6$ ; crystallizes, and may be volatilized without decomposition.

*Brombenzoic Acid*:  $2HIO(C_{14}H_4Br)O_3, ^-BzO_3$ , arises, if bromine be slowly conducted over benzoate of silver; possesses a crystalline appearance; melts at  $100^\circ$ ; sublimes unchanged; sparingly soluble in water, but easily soluble in alcohol and ether.

*Binitrobenzoic Acid*:  $HIO(C_2, 2NO_2, C_2H_2, C_8, C_2H)O_3 = HO, (C_{14}H_3, 2NO_2)O_3$ , is formed, if benzoic acid be boiled one hour with a mixture of fuming sulphuric and fuming nitric acid. Binitrobenzoic acid is precipitated from

the solution by water, and obtained in small crystals by evaporation of the alcoholic solution. Scarcely soluble in water, but rather easily soluble in alcohol and ether; may be sublimed when cautiously heated. Gives, with *potassa*, *soda*, and *ammonia*, crystallizable salts, and with oxide of lead and silver, sparingly soluble salts. If benzoic acid be treated with concentrated nitric acid alone, we obtain *nitrobenzoic acid*, which consists of benzoic acid, and binitrobenzoic acid  $= \text{HO}(\text{C}_{14}\text{H}_4\text{NO}_4)\text{O}_3$ .

*Nitrobenzoic Acid* is further formed by the action of nitric acid upon bitter almond oil, cinnamon oil, <sup>Nitrobenzoic acid.</sup> cinnamic acid, and *dragon's blood*. Nitrotolinic acid, which is formed by long boiling of tolin with nitric acid, is also probably nitrobenzoic acid. In order to obtain it, we boil benzoic acid several hours with nitric acid, then during the cooling, nitrobenzoic acid separates. From the hot aqueous solution it gives small white crystals; dissolves easily in boiling water, but with difficulty in cold; melts at  $127^\circ$ ; sublimes unchanged; the vapor strongly excites coughing.

If the silver salt be cautiously heated, we obtain nitrobenzid. If the alcoholic solution of nitrobenzoic acid saturated with *ammonia*, and *hydrosulphuric acid*, be boiled, we obtain *benzaminic acid*,  $\text{HO}(\text{C}_{14}\text{H}_4\text{NH}_2)\text{O}_3$ . It exhibits nitrobenzoic acid, in which  $\text{NO}_4$  is replaced by  $\text{NH}_2$ . Apparently benzaminic acid is double, consisting of benzoic acid +  $\text{HO}(\text{C}_{22}\text{2NH}_2\text{C}_2\text{H}_2\text{C}_8\text{C}_2\text{H})\text{O}_3$ ; it thence belongs not to the amid combinations.

If nitrobenzoic acid be warmed with *chloride of phosphorus*, a heavy fluid distils over, which boils at  $265^\circ$ , and, treated with hot potassa solution, gives nitrobenzoic acid, and chloride of potassium; it consists of  $\text{HO}(\text{C}_{14}\text{H}_4\text{NO}_4) \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right.$  it is hence bioxychloride of nitrobenzoyl. It forms with <sup>Bioxychloride of nitrobenzoyl.</sup> ammonia a product which crystallizes in yellow needles.

*Nitrobenzoic acid* combines easily with bases, and expels several acids from their compounds. The salts are mostly soluble in water and alcohol; crystallizable; explode by heating, and leave, when gently warmed, nitrobenzid, under blackening. They are procured either direct, or by double decomposition. If the ammonia salt be a long time fused, we obtain *nitrobenzamid*,  $\text{NH}_2(\text{C}_{14}\text{H}_4\text{NO}_4)\text{O}_2$ , which crystallizes in yellow needles.

*Benzaminic Acid*:  $\text{HO}(\text{C}_{14}\text{H}_4\text{NH}_2)\text{O}_3$ . Crystallizes from the hot saturated aqueous solution in thin, <sup>Benzaminic acid.</sup> short, radiated crystals, which easily dissolve in boiling water, alcohol, and ether; inodorous, and rather sour taste; melts to a clear, colorless fluid; strongly heated it emits a vapor, smelling like benzoic acid. In fuming *nitric acid* it dissolves with a blood red color. *Chlorine* decomposes the acid. It expels

carbonic acid from compounds of the latter, and gives with the alkalis and earths salts easily soluble in water and alcohol, not crystallizable.

*Sulphobenzo-sulphuric Acid*:  $2\text{HO}(\text{C}_{14}\text{H}_4\text{SO}_2)\text{O}_3, \text{SO}_2$ . Corresponds to sulphacetyl-sulphuric acid, and is formed by the action of aqueous sulphuric acid upon benzoic acid. The pasty mass is diluted with water, and the sulphobenzo-sulphuric acid obtained by saturation with baryta, etc. If the aqueous solution be evaporated until the boiling point rises to  $150^\circ$ , the acid stiffens after cooling to a crystalline mass; deliquesces in the damp air; is very permanent, not even decomposed by boiling with concentrated nitric acid. It saturates 2 atoms of base, of which one can be substituted by HO.

#### PAIRED COMBINATIONS OF BENZOYL.

##### 1. CINNYL (CIMMYL):



*Cinnamic Acid* (Zimmtsäure):  $\text{HOCnO}_3$ . It is related to benzoic acid as oxide of cinnamyl to oxide of picramyl (bitter almond oil). It is found in old oil of cinnamon, in Peru balsam, and in tolu balsam, and is produced from oxide of cinnamyl, from cinnamein and styracin. The crystals which are deposited from old cinnamon oil are cinnamic acid, and can be purified by recrystallization. Or we mix an alcoholic solution of Peru balsam with an alcoholic solution of potassa so long as a precipitate is formed; add water to the abfiltered fluid, separate the cinnamein which is deposited, distil off the alcohol, and precipitate the cinnamic acid from the aqueous solution by hydrochloric acid. It is purified by recrystallization or by sublimation. It appears in colorless, pearly leaflets; from the aqueous solution it crystallizes in long, indistinct prisms. In its properties it quite agrees with benzoic acid; it melts at  $120^\circ$ , and boils at  $293^\circ$ ; its vapor is suffocating, and excites coughing. If it be distilled with 4 parts baryta it decomposes into carbonic acid, and cinnamein (cinnamol) and carbonic acid. If instead of baryta pure lime be employed, we obtain benzin. Toward *nitric acid* and *sulphuric acid*, it behaves exactly like benzoic acid. Also the *cinnamic acid salts* resemble those of benzoic acid. They are mostly soluble in water, and are capable of crystallization. The acid, as well as its salts, is converted into benzoic acid if boiled with *peroxide of manganese* or *chromate of potassa* and *dilute sulphuric acid*. The same result follows the action of *chlorine* or chloride of lime; we at first obtain benzoic acid, and by further action chlorbenzoic acid; simultaneously there is also formed a *heavy oil*, of peculiar



aromatic smell. If the cinnamic acid be heated with *chloride of phosphorus*, *bioxychloride of cinnyl*,  $\text{Cn} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right.$  is formed.

*Bioxychloride of Cinnyl* (Cymmylbioxychlorid):  $\text{Cn} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right.$  A fluid boiling at  $262^\circ$ , which decomposes in the damp air into hydrochloric and cinnamic acid. Gives with aqueous ammonia a white crystalline body, *cinnamid* (cimmamid), analogous to benzamid. If this be distilled with cyanide of potassium or of mercury, we obtain oxycyanide of cynnyl,  $\text{Cn} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cy} \end{smallmatrix} \right.$ .

*Binitrocinnamic Acid* (Binitrozimmtsäure):  $\text{HO}(\text{C}_4\text{H}_2, \text{C}_2\text{NO}_4, \text{C}_3\text{H}_2, \text{C}_8, \text{C}_2\text{H})\text{O}_3$ , forms with 1 atom cinnamic acid, the nitrocinnamic acid  $=\text{HO}(\text{C}_{18}\text{H}_6, \text{NO}_4)\text{O}_3$ . It is obtained, if cinnamic acid be carried into cooled fuming nitric acid; it forms crystals, which are purified by recrystallization from boiling alcohol; it much resembles the nitrobenzoic acid, but it requires 327 parts alcohol at  $20^\circ$  for solution, whereby it differs from that acid. If it be boiled with a little water, it melts to an oily fluid. Nitrocinnamic acid is weak, and forms, with the alkalis, easily soluble neutral salts, and with the other bases salts, some of which are soluble with difficulty, and others insoluble.

Derived radicals of cinnyl. Nitrocinnamic acid.

*Sulphocinnsulphuric Acid* (Sulfozimmtsulfensäure):  $2\text{HO}(\text{C}_4\text{H}_2, \text{C}_{14}\text{H}_4, \text{SO}_2)\text{O}_3 \text{ SO}_3$ , is obtained like sulphobenzoe-sulphuric acid. Remains, after evaporation of the aqueous solution in a vacuum, as an amorphous mass of pale-yellow color, which becomes moist in the air, and is easily soluble in water and alcohol. By spontaneous evaporation of the alcoholic solution it separates in long prisms, which contain 6 atoms water. The acid saturates 2 atoms of base. The pure acid, as well as the alkali salts, give a precipitate only with vinegar of lead and nitrate of protoxide of mercury.

Sulphocinnsulphuric acid.

*Myroxylic Acid* (Carbobenzoic Acid):  $\text{HO}, \text{C}_{15}\text{H}_6\text{O}_3 = \text{HO}(\text{CH}, \text{C}_{14}\text{H}_5)\text{O}_3$ . This acid is obtained by the action of an alcoholic solution of potassa upon cinnamein with cinnamic acid and peruvine. If the alkaline solution be mixed with hydrochloric acid, there separates a mixture of cinnamic and myroxylic acid. From the hot aqueous solution, the cinnamic acid is first deposited, and, by evaporation, the myroxylic acid. It quite equals benzoic acid, but melts even at  $109^\circ$ ; first boils at  $250^\circ$ , and is more easily soluble in water.

Myroxylic acid.

## 2. HIPPURIC ACID:



*Hippuric acid* is found in the urine of the horse, the cow, and, in small quantity, also in human urine.

Hippuric acid.

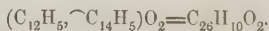


Benzoic acid, as well as cinnamic acid, changes in animal bodies into hippuric acid, which is found in urine. By the action of acids and alkalies, hippuric acid decomposes into glycol and benzoic acid. If the elements of 2 atoms water come to the pairing of hippuric acid  $\text{NC}_4\text{H}_3\text{O}_2$ , we obtain glycol  $=\text{NC}_4\text{H}_5\text{O}_4$ . Horse urine evaporated to  $\frac{1}{8}$  is mixed with hydrochloric acid, the precipitate pressed out and boiled with water and milk of lime; then it is filtered, and a solution of alum added to the filtrate, until the alkaline reaction vanishes. Into the fluid cooled to  $40^\circ$ , we bring bicarbonate of soda, until no more precipitate is formed, and from the abfiltered solution the hippuric acid is precipitated by nitric acid, and then purified by recrystallization from boiling water and treatment with animal charcoal. Crystallizes in well-formed quadratic prisms; it is deposited from the concentrated salt solution upon the addition of acid, always in distinct long needles. Reacts strongly acid, but possesses no sour taste; it fuses by a gentle heat, and stiffens to a crystalline mass; it requires 400 parts cold water for solution; easily soluble in boiling water and alcohol. By *dry distillation* decomposes into benzoic acid and benzoate of ammonia; immediately an oily fluid distils over, which by cooling stiffens and behaves like a resin; by strongly heating, hydrocyanic acid is evolved, and carbon remains as residue. Slowly heated with an excess of lime, ammonia and hydrobenzid go over. Heated with *peroxide of manganese* and *sulphuric acid*, we obtain carbonic acid, ammonia, and benzoic acid. If hippuric acid be boiled with water, and *superoxide of lead*, the whole stiffens to a crystalline mass of benzamid.

The *salts of hippuric acid* resemble those of benzoic acid; they mostly crystallize; with potassa it gives a neutral and an acid salt.

To the paired combinations of benzoic acid, belongs also *benzilic acid*  $=\text{HO}, \text{C}_{14}\text{H}_6\text{O}_2 \wedge (\text{C}_{14}\text{H}_5)\text{O}_3$ , mentioned *page 225*.

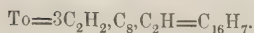
### 3. BENZON:



*Benzon* is formed by dry distillation of neutral benzoate of lime. The obtained distillate is a mixture of hydrobenzid, naphthalin, and benzon. This is submitted to distillation, and when the boiling point arises to  $250^\circ$ , the receiver is changed. What now goes over, is a mixture of benzon, and naphthalin; at  $-20^\circ$  the naphthalin is deposited. Benzon is a colorless oil, flowing with difficulty, and of an empyreumatic, not disagreeable odor; lighter than water; boils at  $250^\circ$ . *Nitric acid*, *potassa*, and *chlorine* appear not to change it. By *sulphuric acid* it is decomposed.

## THIRD MEMBER.

## TOLUYL:



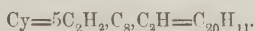
*Hydrate of Toluylic Acid:*  $\text{HO}, \text{ToO}_3$ . This acid is obtained, if hydrocymyd (Cymin) be boiled several days with 4 to 5 parts dilute nitric acid (*vide* Hydrocymid). After cooling, the liquid in the retort is filled with white crystals of toluylic acid, with which a small quantity of nitrotoluylic acid is admixed. We boil the deposited acid with milk of lime, filter, and, after cooling, precipitate with hydrochloric acid; we repeat this operation, until the separated acid appears quite white. It is then dissolved in baryta water, the solution evaporated to dryness, and the residue treated with cold water, which leaves the nitrotoluylate of baryta undissolved. From the hot saturated aqueous solution, the acid is deposited in perfectly white needles; very easily soluble in wood-spirit, alcohol, and ether; inodorous and tasteless. The salts agree with those of benzoic acid. Distilled with an excess of baryta, we obtain tolin and carbonic acid.

*Nitrotoluylic acid* is a compound of binitrotoluylic with toluylic acid. It is formed by the action of fuming nitric acid upon toluylic acid, and upon cymin. It crystallizes from the alcoholic solution in splendid pale-yellow rhombic prisms.

The *baryta salt* is deposited from the hot, aqueous solution in radiated crystals.

## FIFTH MEMBER.

## CUMINYL:



*Hydrate of Cuminylic Acid (Cuminic Acid):*  $\text{HO}, \text{Cuminic acid. CyO}_3$ . Pure potassa is heated to melting in a retort, and then upon it is brought, in drops, Roman cumin oil. The oil becomes immediately solid, whilst the cymin distils over (*vide* Cumin Oil). After the decomposition is terminated, the mass is dissolved in water, and from the solution the acid is precipitated by hydrochloric acid and purified by recrystallization from the alcoholic solution. Crystallizes in white, very beautiful prismatic tables, which taste sour, and possess a peculiar odor; melts at  $92^\circ$ , and boils at  $250^\circ$ ; sublimes in beautiful needles often an inch long. Sparingly soluble in boiling water, but easily soluble in alcohol and ether. Decomposes by distillation with lime into cumin and carbonic acid. It agrees in its acid properties with benzoic acid; it expels carbonic acid from its compounds, and

gives with oxides of metals well-characterized salts, which are obtained direct, as well as by double decomposition.

**Bioxychloride of cuminyll.** *Bioxychloride of Cuminyll*:  $\text{Cu} \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix} \right\}_2$  is formed, if cuminic acid is distilled with chloride of phosphorus, as well as by the action of dry chlorine gas upon anhydrous cumin oil. Appears as a yellowish fluid, heavier than water, of strong penetrating odor, decomposes in the damp air into cuminic and hydrochloric acid.

*Bioxybromide of cuminyll* resembles the chlorine compound.

**Binitro-cuminic acid.** *Binitro-cuminic Acid*:  $\text{HO}(\text{C}_2\text{NO}_4, 4\text{C}_2\text{H}_2, \text{C}_8, \text{C}_2\text{H})\text{O}_3 = \text{HO}(\text{C}_{20}\text{H}_9, 2\text{NO}_4)\text{O}_3$ , is formed, when cuminic acid, in small quantity, is brought into a mixture of fuming sulphuric and nitric acid. Crystallizes from the alcoholic solution in shining leaflets; not sour. If cuminic acid be treated with fuming nitric acid alone, we thus obtain a combination of binitrocuminic and cuminic acid, or the so-named *nitro-cuminic acid*, which forms in yellowish-white crystals; it combines with bases.

*Salt-like Combination of the Oxides of the Methyl Group with the Acids of the Benzoyl Group.*

**Combinations of oxide of methyl.** *Benzoate of Methyl*:  $\text{MeO}, \text{BzO}_3$ ; an oily, colorless, balsamic smelling fluid; insoluble in water, but easily soluble in alcohol, and ether; sp. gr. 1.10; boils at  $198.5^\circ$ ; conducted over redhot lime, we obtain benzin and other products.

**Combinations of oxide of ethyl.** *Benzoate of Ethyl*:  $\text{AeO}, \text{BzO}_3$ . Colorless oily fluid, of slight odor and suffocating taste; insoluble in cold water, easily soluble in alcohol and ether; boils at  $209^\circ$ ; sp. gr. 1.0559; burns with very sooty flame. Led over heated hydrate of potassa, we obtain benzoate, and acetate of potassa under evolution of hydrogen.

*Nitrobenzoate of Ethyl*: Crystallizes from the warm etheric solution in distinct crystals, which melt at  $70^\circ$ , and boil at  $300^\circ$ ; volatile.

*Binitrobenzoate of Ethyl*: Crystallizes from the alcoholic solution in long, slender, shining, scarcely colored needles.

*Cinnamate of Ethyl*:  $\text{AeO}, \text{CnO}_3$ . Clear, colorless fluid, of agreeable, aromatic odor, like cinnamon. Boils at  $260^\circ$ ; sp. gr. 1.13. Is found in Peru balsam.

*Nitrocinnamate of Ethyl*: Crystallizes; melts at  $136^\circ$ , and decomposes at  $300^\circ$ .

*Hippurate of Ethyl*: Crystallizes in long, unctuous, white needles of silky lustre; inodorous, of sharp taste, like turpentine

oil; scarcely soluble in water, but easily soluble in alcohol and ether; sp. gr. 1.043; melt at  $44^{\circ}$ . Submitted to distillation, the compound decomposes; heated in the air, vapor of benzoic acid escapes.

*Toluylate of Ethyl* appears as an agreeably smelling fluid, which boils at  $228^{\circ}$ .

*Nitrotoluylate of Ethyl*: Crystallizes in pale-yellow, aromatic-smelling crystals, which fuse upon the water bath.

*Cuminate of Ethyl*. A colorless fluid, lighter than water, of agreeable, apple-like odor; boils at  $240^{\circ}$ ; insoluble in water, but miscible with alcohol and ether in all proportions; heated with a solution of potassa, it decomposes into cuminic acid and alcohol.

All kinds of ether are obtained if hydrochloric acid gas be conducted into the alcoholic solution of the corresponding acid, as well as by the action of alcohol upon the oxychlorine compounds of the radicals; thus bioxychloride of benzoyl in contact with alcohol gives benzoate of ethyl.

#### APPENDIX TO THE ACIDS OF THIS GROUP.

##### ALOETINIC ACID AND CHRYSAMMINIC ACID:

Aloetic Acid:  $C_{16}H_4N_2O_{13} = HO, (C_2(NO_4)_2, C_2H_2, C_{10}, C_2H)O_4(?)$  Aloetic acid.

If one part aloes be gently warmed with 8 parts of dilute nitric acid, we obtain a dark blue or emerald solution, and by farther heating a violent action commences, accompanied by strong evolution of gas. If, after the first action terminates, the residue be heated a few days nearly to boiling, and the yet present nitric acid mostly distilled off, there remains, by mixing the residue with water, a greenish-yellow mass, consisting of shining scales, a mixture of aloetic and chrysamminic acid. If the mixture be treated with carbonate of potassa, the aloetic acid dissolves, whilst the chrysamminate of potassa mostly remains behind. From the alkaline solution the aloetic acid is precipitated by an acid. It appears as an insoluble yellow powder, without a trace of crystallization, and produces salts, the most of which are easily soluble. If the aqueous solution of the potassa salt be slowly evaporated, we obtain long, ruby, shining crystal needles.

Chrysamminic Acid:  $HOC_{14}HN_2O_{11} = HOC_2(NO_4)C_{10}, C_2HO_3(?)$ .

By being treated with strong nitric acid, aloetic acid is converted into chrysamminic acid. This latter acid we obtain when chrysamminate of potash (see Aloetic Acid) is dissolved in boiling water, and the solution is mixed with nitric acid. A greenish-yellow powder, consisting of small, shining scales, which when suspended in water show by moving a peculiar white lustre; of bitter taste, insoluble even in

Chrysamminic acid.



boiling water, but rather easily soluble in alcohol, ether, and mineral acids.

By being slowly heated in the air, it fuses to a brown liquid, with strong evolution of gas; quickly heated, it powerfully detonates, and burns with a luminous, sooty flame; it dissolves in *fuming nitric acid*, without decomposing; chlorine does not act upon the acid in the cold; if it be treated with an excess of caustic potassa, we obtain, without evolution of ammonia, a brown solution which becomes darker by heating. If the solution be mixed with an acid, carbonic acid escapes, and a brown precipitate is produced, consisting of *aloeresinic acid* =  $C_{12}H_4N_2O_9$ . If

Aloeresinic acid.

chrysamminic acid be treated with a boiling solution of *sulphide of potassium* and *pure potassa*, there are

deposited from the solution in cooling crystal needles, which appear blue in transmitted and red in reflected light. This body is

Hydrochrysamid.

*hydrochrysamid* =  $C_{14}H_6N_2O_6$ ; it is insoluble in water, and in alcohol little soluble, with blue color; it is also obtained if chrysamminic acid be added to a

boiling solution of chloride of tin. The *chrysamminic acid salts* are not easily soluble, and crystallize from water in small, gold-green scales, which by being heated powerfully detonate. If a solution of the acid be boiled with aqueous ammonia, in cooling there separate from the purple-red fluid needles of *chrysammina-*

Chrysamminamid.

*amid*, which appear reddish brown by transmitted, and green by reflected light, and possess a metallic lustre; it consists of  $C_{28}H_{10}N_7O_{24}$ . This body appears

also to be produced when ammonia gas at  $100^\circ$  is conducted over chrysamminic acid, water being also produced. If *dilute hydrochloric* or *sulphuric acid* be added to a solution of chrysamminamid, in cooling, there are deposited dark olive-green needles of

Amido-chrysamminic acid.

*amido-chrysamminic acid* =  $C_{28}H_8N_6O_{22}$ ; if the same be treated with boiling nitric acid, or with potassa, chrysamminic acid is produced. From the dark

purple aqueous solution the amido-chrysamminic acid is precipitated by acids.

### *Fifth Group.*

The fifth group includes

- a. The Etheric Oils and Camphors, and
- b. The Resins.

### THE ETHERIC OILS AND CAMPHORS.

Occurrence of volatile oils.

All plants and parts of plants which are distinguished by a strong odor owe that property to peculiar smelling compounds, which, on account of their phy-

sical properties and resemblances are named *volatile* or *etheric oils*; they are allied in many respects to the compounds of the benzyd and phenol group, which also bear the name of *empyreumatic oils*, because they are mostly the products of dry distillation. Many substances which on account of their occurrence and physical properties might be classed with the volatile oils, must, on account of their chemical relations, belong to other compounds already described; as oil of rue, of bitter almonds, of cinnamon, cinnamin, salicylous acid, the oil of *Gaultheria procumbens*, etc.; and those only are here treated which in respect to their constitution and chemical resemblances stand in the same relation as the compounds of the above-treated group, equally if they occur already formed in plants and animals, or are artificially produced by dry distillation, by fermentation, or by other influences. The ethereal oils are most extensively diffused in the vegetable kingdom; many plants contain in all their parts the same oil, others have, as readily appears from the odor, different oils in the roots, leaves, blossoms, and fruit.

*Production of Volatile Oils in general.*—Most of the *volatile oils* are procured by the distillation of plants and parts of plants with water. It is probable that many volatile oils are first produced by the action of water upon peculiar combinations occurring in plants, through fermentation, or a similar process, as the oil of bitter almonds from the amygdalin. Although the boiling point of all volatile oils lies higher than that of water, yet they, on account of the common property of their volatile matter, distil over, and evaporate below the boiling point, with aqueous vapor, which is saturated with that of the oils. As the volatile oils are not insoluble in water, we are to consider that, in their production, the quantity of water, which distils over with the oils, is not sufficient to retain the oils in solution; for this latter object we may employ higher and smaller distillation-vessels, and raise the boiling point by the addition of common salt. Most generally, oil is obtained when compressed aqueous vapor is conducted through vegetable matter. Many vegetable substances contain so little oil that the same water must be repeatedly distilled over new portions of them, before oil is extracted.

If the vegetable matter be rich in volatile oil, the latter can be procured by expression, as lemon-oil and orange-oil from the peel of the fresh fruit. Often, after making incisions, a portion of these oils flows of itself out of different plants—a mixture of volatile oils with resins, which mixture is properly called balsams; if this be distilled with water, the resin remains behind, whilst the oil itself volatilizes. (Turpentine, Copaiva Balsam, etc.)

The volatile oils are mixtures.

*The Volatile Oils are Mixtures.*—The volatile oils being procured by simple distillation of plants with water, are almost always a mixture of two, and often of three different oils, of which generally the most volatile are non-oxygenous, whilst the less volatile contain oxygen. If the crude oils be afterwards subjected to distillation, those containing oxygen go over last; the first portions, however, which distil over, are, of course, always a mixture of oxygenous and non-oxygenous oils, and their complete separation can only be effected by chemically acting bodies. If we distil such a mixture over fused hydrate of potash, the oxygenous oils remain behind, mostly, however decomposed, whilst the non-oxygenous distil over; the latter correspond most generally to the formula  $C_{10}H_8 = C_{20}H_{16}$ , and are called *Terebene*, and also *Camphene*.

Properties of the volatile oils.

The volatile oils are only slightly soluble in water, yet the oxygenous are absorbed in larger quantity than the non-oxygenous. The aqueous solutions possess the odor of the oils; they are generally obtained, when the vegetable matter is distilled with a sufficient quantity of water to retain in solution, in the condensed water, the oil, which goes over with the aqueous vapor (*aquæ destillatæ* of the apothecaries). With anhydrous alcohol, the ethereal oils mix in all proportions, hydrous alcohol dissolves them in proportion to its strength (Cologne water, balsamic mixtures, etc. are alcoholic solutions of odoriferous oils). Ether dissolves the volatile oils abundantly; they are completely miscible with the fatty oils. (Adulteration of the volatile oils with anhydrous alcohol, fatty oils, etc.)

### TEREBENE, or CAMPHENE.

General formula:  $C_{10}H_8 = C_{20}H_{16}$ .

*General Relations of Terebenes.*—Whether the terebenes correspond to the formula  $C_{10}H_8$ , or to  $C_{20}H_{16}$ , is difficult to decide, since for each view equally good reasons can be given; in the former case they correspond to 2 volumes of gas, in the latter to 4 volumes. From the behavior of terebenes to the hydrogen acids of the halogens, it appears that a few correspond to the formula  $C_{20}H_{16}$ , others consist of  $C_{10}H_8$ , thus hydrochloric acid gives with oil of turpentine a combination consisting of  $C_{20}H_{16}, HCl$ , whilst the hydrochlorate of lemon-oil corresponds to the formula  $C_{10}H_8, HCl$ .

But the agreement of the boiling point and specific gravity of the gases, speak in favor of the polymerism of these combinations. The difference of the terebenes is farther shown by their different power of rotation of polarized light, since some turn the light to the left, some to the right, and still others do not in the least bend it from its course. The terebenes are farther distinguished by being modified by the action of heat, and also by treatment



with acids and bases, being converted into isomeric or polymeric compounds (without changing the percentage of their constitution), whose difference from the original substance can often only be known by the changed polarization.

*Behavior of the Terebenes to water.*—*Formation of Camphor.*—Many, indeed probably all compounds belonging to the class of the terebenes, possess the capability of combining under certain conditions with water, and thereby being converted partly into fluid, partly into solid, volatile, crystallizable compounds, called *camphors*. Thus, for example, the oil of turpentine, by receiving the formula  $C_{20}H_{16}$ , gives three combinations with water =  $C_{20}H_{16}, HO$ ;  $C_{20}H_{16}, 4HO$ , and  $C_{20}H_{16}, 6HO$ . The last compound loses even in the dry air 2 atoms  $HO$ , and goes over into the compound with 4 atoms  $HO$ . It is not probable that this substance contains water as such, and by known corresponding facts it may be supposed that, by the absorption of hydrogen from the water, radicals rich in hydrogen arise, which unite with oxygen. Accordingly, the formula for the first compound is  $C_{20}H_{17}O$ , for the second  $C_{20}H_{20}O_4$ , and for the third  $C_{20}H_{20}O_4 + 2aq$ . But if we take the formula  $C_{10}H_8$  for turpentine oil, the first compound consists of  $(C_{10}H_8 - C_{10}H_9)O$ , the second of  $C_{10}H_9O + HO$ , and the third of  $(C_{10}H_9, O)_2HO + aq$ . If these bodies be distilled with anhydrous phosphoric acid, we again obtain an oil corresponding to the original constitution.

Behavior of the terebenes to water.

*Behavior of the Terebenes to the Hydrogen Acids of the Halogens.*—As the terebenes combine with water, even so they also combine with the anhydrous hydrogen acids of the halogens. Oil of turpentine turns polarized light to the left. If we slowly conduct hydrochloric acid gas in the cold into oil of turpentine, crystals are deposited, which consist of  $C_{20}H_{16}, HCl = C_{20}H_{17}, Cl$ . These crystals still possess the same power of rotation as the original oil. Simultaneously with the crystals a fluid compound is produced, and the more fluid the higher the temperature at which the hydrochloric acid acts upon the oil. But this compound no longer possesses the power of rotation.

Behavior of terebenes to hydrogen acids.

If the solid compound be distilled with caustic potassa, an oil is obtained, which has the same constitution as oil of turpentine, a solid also is again produced with hydrochloric acid, but it behaves indifferently towards polarized light; it is therefore no longer original oil of turpentine, but an isomeric modification of that substance. If the fluid compound be treated in the same manner, an oil is obtained, which possesses no power of rotation, and unites with hydrochloric acid to form another fluid compound. Similar behavior is also observed in the other terebenes.

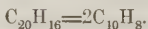


Behavior of  
terebenes to  
oxygen.

Formation of  
resin.

*Behavior of the Terebenes to Oxygen.*—The terebenes absorb oxygen from the air, acquire thereby the property of destroying, like chlorine, organic coloring matter, assume a dark color, are condensed, lose in the same proportion their volatility, and are at last completely transformed into resins. This transformation into resin does not, however, consist of simple oxidation, but of a partial oxidation of the hydrogen, whereby arise radicals poor in hydrogen, which radicals then oxidize. Simultaneously are the terebenes converted into polymeric compounds. The resins stand therefore to the oils in a relation similar to that, for instance, of benzoic acid to oil of bitter almonds, or the acids of the formyl series to the oxides of the methyl series, and, in fact, most resins possess acid characteristics, whilst the terebenes must be regarded as basic compounds. Thus silvinic acid, which arises from oil of turpentine, consists of  $C_{40}H_{30}O_4$ . Without doubt,  $C_{40}H_{30}O_2$  arises first, since 2 atoms of hydrogen escape from 2 atoms of oil of turpentine, and afterwards, by farther oxidation,  $C_{40}H_{30}O_4$  is formed. When *nitric acid* in a concentrated state acts upon the terebenes, it decomposes them with violence, rising to inflammation; if the acid be dilute, we obtain new acids, as terebenic, terochrynic acid, etc. Simultaneously from the oil of turpentine are also volatile acids of the formyl series produced, as acetic and butyric acid. *Metallic oxides*, as oxide of copper, vermilion, are often reduced to metals by boiling with the terebenes. *Chlorine* and *bromine* in like manner act with violence upon the terebenes, and produce derived compounds, whilst hydrogen acids are evolved. *Chloride of tin* and of *antimony* are often reduced to metals. *Iodine*, when brought in contact with the terebenes, produces a slight decrepitation, etc.

#### OIL OF TURPENTINE.



The oil of turpentine, which is obtained by distillation of turpentine (a mixture of oil of turpentine and colophon, which flows from various species of *Pinus*, *Pinus silvestris*, *Abies, maritima*, *Picea*, *Mughsis*, etc., partly spontaneously, and partly from incisions) with water, exhibits in a pure state a colorless, thin-flowing liquid, of a peculiar disagreeable smell, and burning taste; insoluble in water, easily soluble in anhydrous alcohol and ether; sp. gr. 0.890; boiling point  $156^\circ$ . The vapor of the oil when inspired produces wakefulness, increases the pulse, and causes difficulty in passing urine. If a small quantity be taken internally, the urine assumes a violet smell. Crude oil of turpentine generally reacts acid, and contains oxygen, formic and succinic acid. It turns polarized light to the left. If oil of turpentine be distilled over an open fire, its power of rotation increases; but if the distillation

occur over pulverized slate-stone, that power is lessened, and the turpentine acquires the property of dissolving caoutchouc in greater quantity than before.

*Terpinol*:  $C_{20}H_{17}O = C_{20}H_{16}HO$ . This is obtained if some acid be added to terpin (turpentine-camphor) in aqueous solution, or the terpin be distilled with hydriodic acid. A colorless fluid, strongly refracting light; of agreeable odor; boils at  $168^{\circ}$ ; sp. gr. 0.852.

*Terpin* (Turpentine-camphor): *anhydrous* =  $C_{20}H_{20}O_4 = C_{20}H_{17}O_3HO$ ; *hydrous* =  $C_{20}H_{22}O_6 = C_{20}H_{20}O_4 + 2aq = (C_{20}H_{17}O_3HO) + 2aq$ . The *anhydrous* combination is formed, when hydrous oil of turpentine is exposed a long time to a temperature of  $50^{\circ}$ , or when the hydrous oil is fused at  $100^{\circ}$ . It crystallizes in rhomboidal prisms, and tufted united needles; fuses at  $103^{\circ}$ , and sublimates like benzoic acid; evaporates in the flame of a candle without kindling; dissolves in 200 parts of cold and in 22 parts boiling water; easily soluble in alcohol, ether, fats, and volatile oils.

The *hydrous compound* is best obtained if 8 parts oil of turpentine, 2 parts nitric acid of 1.25 sp. gravity, and 1 part alcohol of 80 per cent. are intimately mixed by repeated shaking, and the mixture then left at rest in a temperature of 20 to  $25^{\circ}$ . Crystallizes in rhombohedral prisms, and behaves towards water, alcohol, and ether, like the anhydrous compounds.

*Hydrochlorate of Oil of Turpentine* (Artificial Camphor):  $C_{20}H_{17}Cl = C_{20}H_{16} + HCl$ . Oil of turpentine is saturated in the cold with hydrochloric acid gas; after a little time crystals are deposited, which are purified by pressing. White prisms, which smell like common camphor; fuses at  $115^{\circ}$ , and boils at  $165^{\circ}$ ; insoluble in water, soluble in 3 parts alcohol.

If pulverized terpin be treated with hydrochloric acid gas, we obtain a brownish liquid (accompanied by evolution of heat), from which, after a little time, a crystalline body is deposited, which is also formed when we lead hydrochloric acid gas into terpinol. This body crystallizes from the cold alcoholic solution in thin leaves of mother-of-pearl lustre, which fuse at  $45^{\circ}$ ; easily dissolves in alcohol, and consists of  $C_{20}H_{18}Cl_2 = C_{20}H_{17}Cl + HCl$  (?). If this compound be boiled several days with water, terpinol is obtained.

*Hydrobromate of Turpentine Oil*:  $C_{20}H_{17}Br$ . From turpentine oil, saturated with hydrobromic acid gas, crystals are deposited in the cold, which, by repeated crystallization out of alcohol are purified. It entirely agrees with the hydrochlorate of turpentine oil. The alcoholic solution, when exposed to the air, becomes red.

*Hydriodate of Oil of Turpentine*:  $C_{20}H_{17}I$ . If hydriodic acid be conducted into oil of turpentine, a dark-red fuming fluid is pro-

duced, which becomes clear after treatment with potash-lye, and alcohol, or mercury; sp. gr. 1.5097; is quickly decomposed in the air, whilst iodine is deposited. There also appears to exist a compound consisting of  $C_{20}H_{18}I_2$ .

*Tereben*:  $C_{20}H_{16}=C_{10}H_8$ . If oil of turpentine be mixed cautiously, and in small quantities with sulphuric acid, a powerful heat is produced, which causes the tereben mostly to distil over. At a higher temperature colophon goes over. If we let hydrochloric acid act upon oil of turpentine, we obtain besides hydrochlorate of turpentine oil, the hydrochlorate of tereben, and the more is obtained, the higher the temperature. Tereben possesses an agreeable thyme-like odor; boils at  $156^\circ$ . Power of rotation = 0.

Tereben combines with *hydrochloric acid* in two proportions, forming  $C_{40}H_{33}Cl$ , and  $C_{20}H_{17}Cl$ ; the same compounds are formed by hydriodic and bromic acid. They possess no power of rotation, and appear as volatile, colorless liquids (fluid, artificial camphor).

*Camphilen*:  $C_{20}H_{16}=C_{10}H_8$ , is obtained when hydrochlorate of turpentine oil is conducted over glowing lime. Fluid; gives, with hydrochloric acid, a solid compound. Power of rotation = 0.

If we distil the compound  $C_{20}H_{18}Cl_2$ , which is obtained by the action of hydrochloric acid upon terpin, with caustic potassa, or if we distil terpin with anhydrous phosphoric acid, we obtain an oil smelling like rosemary.

*Terebilen*:  $C_{10}H_8$ . Thus is called the oil, which is obtained when hydrochlorate of tereben (fluid, artificial camphor) is distilled with lime. Gives, with hydrochloric acid, a fluid compound. Rotation = 0.

*Chlorcamphen*:  $C_{20}H_{12}Cl_4$ , is obtained by the action of chlorine upon hydrochlorate of turpentine oil, and in its properties it agrees with the latter substance. Fuses at  $110$  to  $115^\circ$  without volatilizing.

Rotation = 0.

*Chlortereben*:  $C_{20}H_{12}Cl_4$ . A glutinous mass, which is obtained by the action of chlorine upon tereben.

*Bromtereben*:  $C_{20}H_{12}Br_4$ , arises in like manner. Fluid, sp. gr. 1.978. Rotation of both = 0.

*Chlorturpentin*:  $C_{20}H_{12}Cl_4$ . By the introduction of chlorine into the oil of turpentine, we obtain a ropy, colorless fluid, of a peculiar camphor-like odor, and sweetish bitter taste. Power of rotation to the right.

*Bromturpentin*:  $C_{20}H_{12}Br_4$ , arises by the action of bromine upon oil of turpentine. A dark-red, thick, glutinous fluid.

*Colophon*:  $C_{40}H_{32}=C_{20}H_{16}$ . In a balloon kept cool, we intimately mix 20 parts of oil of turpentine, and 1 part sulphuric acid, and, after twenty-four hours, submit the dark-red, glutinous mixture to distillation; at first tereben goes over, and afterwards colophon.



The latter is colorless, if the transmitted rays of light come to the eye; but if the bottle containing colophon be held somewhat high, and a dark body be placed behind the bottle, the transmitted light diminishes and the colophon appears a dark indigo-blue. This *dichromism* is found in all compounds of colophon, but if the compound be yellow, the blue color is converted into green. Odor peculiar; sp. gr. 0.940; boils at  $315^{\circ}$ . Gives, with chlorine, a compound, which consists of  $C_{40}H_{32}Cl_4$ ; combines with hydrochloric acid.

#### CAMPHOR-OIL, BORNEO CAMPHOR, and COMMON CAMPHOR.

*Camphor Oil* (Valerian Oil, Laurel Oil):  $C_{20}H_{16}$  Camphor oil.  
 $=C_{10}H_8$ . It occurs in the camphor-tree (*Dryobalanops camphora*), growing in Sumatra and Borneo, and also in the valerian root, in the laurel-berry, etc. We also obtain camphor oil when the Borneo camphor,  $C_{20}H_{18}O_2$ , is distilled with anhydrous phosphoric acid. A colorless oil, of agreeable odor like cajeput oil; sp. gr. 0.945; boils at  $160^{\circ}$ . Exposed to the air, it absorbs oxygen, and is converted into common camphor; with hydrochloric acid it gives a crystallizable compound.

*Borneo Camphor*:  $C_{20}H_{18}O_2 = C_{10}H_9O$ , is found with camphor oil in the camphor-tree, and is formed, if camphor oil (valerian oil) be treated some time with hot potash-lye. Crystallizes in small, colorless, transparent, regular six-sided prisms; smells like common camphor and pepper; floats upon water; fuses at  $198^{\circ}$ , and boils at  $212^{\circ}$ . Little soluble in water, but abundantly soluble in alcohol and ether.

*Cajeput oil*, which comes from the *Melaleuca cajeput*, has the same constitution as Borneo camphor. The crude oil is very thin, completely transparent, of strong aromatic odor, and burning taste; sp. gr. 0.9274; boils at  $175^{\circ}$ ; color green. By distillation, a colorless oil goes over, which boils at  $173^{\circ}$ , whilst a scanty, resinous residue remains. Iodine is dissolved in the oil without explosion.

*Laurus Camphor* (ordinary Camphor):  $C_{20}H_{16}O_2$ . If Borneo camphor be gently warmed with moderately concentrated nitric acid, it is converted into ordinary camphor. This latter may also be formed by the action of nitric acid upon sage oil. It occurs in *Laurus camphora*, and is procured by distillation of the wood with water. Ordinary camphor appears also to occur in crude lavender oil, rosemary, and poley-oil; in the oil of *Mentha viridis*, and *Origanum vulgare*. In its pure state it appears as a white, semi-transparent, crystalline mass, of strong peculiar odor, and bitter, cooling taste. Crystallizes in colorless, transparent, octohedrons from the hot, saturated, alcoholic solution. Can be pulverized only after the addition of alcohol; fuses at  $175^{\circ}$ ; boils



at  $204^{\circ}$ ; sp. gr. 0.9856. Dissolves in 1000 parts water, and is again precipitated by potassa, but not by ammonia, or soda. If small pieces of camphor be thrown upon water, in consequence of the ordinary evaporation of the camphor, the water assumes a whirling motion, but the smallest portion of oil brought upon the surface of the water, prevents this appearance. 100 parts alcohol of 0.806 specific gravity dissolves 120 parts camphor; it is farther easily soluble in ether, wood-spirit, sulpho-carbonic acid, acetone, and hydrate of acetic acid; can be fused with sulphur and phosphorus, burns with a strong sooty flame.

If the vapor of camphor be conducted over *red-hot iron*, we thus obtain naphthalin, and a fluid consisting of  $C_{16}H_8$  (cinnamin?).

Brought in contact with *lime heated to redness*, it is decomposed, forming *camphron*—a light liquid, consisting of  $C_{30}H_{22}O$ , odor like camphor. Heated with *potash-lime*, it is converted into *campholic acid*,  $C_{20}H_{17}O_3$ ; distilled with anhydrous phosphoric acid, it separates into water and *cymin*  $C_{20}H_{14}$  (page 239), and if it be intimately mixed with *alumina*, and submitted to distillation, an aromatic oil is formed; odor like that of rosemary. *Nitric acid* converts it into camphoric acid. If *chlorine gas* be conducted into a solution of camphor in *protochloride of phosphorus*, an oily substance is obtained, which must consist of  $C_{40}H_{25}Cl_7O_2$ . *Protobromide of phosphorus* behaves in the same manner. With *bromine*, camphor forms garnet-red crystals  $C_{20}H_{16}O_2 + Br_2$ .

Camphin.

If a mixture of iodine and camphor be distilled, we obtain colophin, carvacrol, and *camphin*, together with evolution of iodide of hydrogen. *Camphin* consists of  $C_{18}H_{16}$ , a colorless, light liquid of pleasant odor; sp. gr. 0.827; boils at  $167^{\circ}$ , and gives, with chlorine, a compound  $= C_{18}H_{13}Cl_3$ ; as residue a mixed, resinous body remains.

*Behavior of Camphor to the Acids.*—Camphor rapidly absorbs *sulphurous acid gas* in different proportions according to the temperature and pressure; at  $2^{\circ}$  and 650 milligrammes pressure, 100 parts camphor absorb 72 parts  $SO_2$ ; in the air the acid escapes. Camphor also unites with *hyponitrous acid*  $NO_2$ , and with *hydrochloric acid gas*. At  $0^{\circ}$  2 atoms of camphor absorb 1 atom of hydrochloric acid. By slow action *anhydrous sulphuric acid* changes camphor into a brownish mass, from which, by the addition of water the camphor is again deposited; 1 part *fuming nitric acid* dissolves 8 parts camphor without decomposition, and water again precipitates it. *Fluor-cilicium gas* and *hydrosulphuric acid* are without action.

*Campholic acid.* *Campholic Acid:*  $HO, C_{20}H_{17}O_3$  Vapor of camphor is conducted over a mixture of hydrate of potash and lime heated to  $300$  or  $400^{\circ}$ , the mass after cooling is boiled with water, and from the filtered solution campholic acid is precipitated

by an acid. Crystallizes from the alcoholic solution; insoluble in water, easily soluble in alcohol and ether; fuses at  $80^{\circ}$ ; boils at  $250^{\circ}$ ; volatile without change; odor aromatic; reddens litmus feebly and completely neutralizes bases. Isomeric with camphor is *wormwood oil*,  $C_{20}H_{16}O_2$ . Occurs in the plant *Wormwood oil*. *Artemisia absinthium*. If the crude oil be rectified a few times over burnt lime, the oil is procured colorless; boils at  $205^{\circ}$ , and, by distillation with anhydrous phosphoric acid, separates into water and *cymen*.

*Lemon Oil*:  $C_{20}H_{16}$ , occurs in the rind of *Citrus medica*, and is obtained by expression. In a pure state a colorless, thin-flowing liquid; of pleasant lemon odor, and burning taste; sp. gr. 0.846; boils at  $165^{\circ}$ . Power of rotation to the right. With water, it gives *lemon camphor*  $= C_{20}H_{22}O_6$ , which, by being heated, loses 2 atoms of water. It gives, with *hydrochloric acid*, a solid and a fluid compound; the solid consists of  $C_{20}H_{18}Cl_2 = C_{20}H_{16} + 2HCl$ . Both compounds possess no power of rotation. *Citren* and *citrilen* are the names given to the oils, which are obtained by the distillation of the hydrochloric acid compounds with lime.

*Bergamot oil* is procured by expressing the peel of the bergamot (*Citrus bergamium*); the crude oil appears to consist of  $C_{20}H_{16} + 2HO$ ; if it be distilled with anhydrous, phosphoric acid, an oil is obtained consisting of  $C_{20}H_{16}$ , which agrees with lemon oil in respect to its behavior to water and to hydrochloric acid. The hydrochloric acid compounds must consist of  $3C_{20}H_{16} + HCl + HO$ . From lemon oil as well as from oil of bergamot at low temperature, a solid is precipitated, which must consist of  $C_{15}H_5O_5$ .

*Orange Oil*:  $C_{20}H_{16}$ , occurs in the peel of the *Citrus aurantium*. It gives with hydrochloric acid a solid and a fluid compound. Power of rotation *right*.

*Orange-blossom Oil* (*Oleum neroli*). A thin oil of very agreeable odor; it is procured by distilling orange-blossoms with water. It is said to consist of two oils.

*Copaiva Oil*:  $C_{20}H_{16}$ , is obtained by the distillation of copaiva balsam with water; a colorless, thin, aromatic oil; sp. gr. 0.885; boils at  $245^{\circ}$ . Rotation to the left. Insoluble in water; in all proportions miscible with anhydrous alcohol and ether. With hydrochloric acid it gives a solid compound  $= C_{20}H_{16} + 2HCl$ , and a fluid compound.

*Elemi oil* and *olibanum oil* deserve mention; they are obtained by distillation of elemi-resin, and olibanum-resin, with water.

*Ocotea oil* occurs in Demara, under the false name of laurel oil. With water it gives a camphor  $= C_{20}H_{20}O_4$ .

*Caruen* is the non-oxygenous oil of caraway (*Carum carui*). It is obtained when the crude caraway oil is distilled with hydrate of

potassa (see Cervacrol, p. 200). It gives with hydrochloric acid a solid compound  $=C_{20}H_{18}Cl_2$ .

*Juniper-berry Oil.* The oil obtained by distilling green juniper berries with salt water is a mixture of two isomeric oils, of which one is more volatile than the other. If we add caustic potassa to juniper-berry water, a camphor is precipitated, which consists of  $C_{20}H_{20}O_4$ .

*Sabine-tree oil* occurs in *Juniperus sabina*.

*Petersilien Oil.* The oil obtained by distillation of parsley-seed (*Apium petroselinum*) is a mixture of an oxygenous and a non-oxygenous oil. If the crude oil be dissolved in water, after a few days the *petersilien camphor* is deposited, it must consist of  $C_{12}H_7O_4$ .

*Clove Oil.* The crude oil of cloves consists of caryophyllic acid (see p. 220), and an indifferent oil, which boils at  $143^\circ$ .

*Clove Camphor:*  $C_{20}H_{16}O_2$ . If cloves (*caryophyllus aromaticus*) be digested with alcohol, after a little time crystals are deposited, which are soluble in water; fuse at  $330^\circ$ , and volatilize at  $290^\circ$ ; it dissolves with blood-red color in sulphuric acid.

*Cubeba oil* occurs in *Piper cubeba*; smells and tastes like camphor; gives with hydrochloric acid a solid compound, which must consist of  $C_{30}H_{24} + 2HCl$ . In the cold, *cubeba camphor* is deposited from cubeba oil.

*Pepper oil* occurs in black pepper.

*Birch oil* occurs in the bark of the *betula lenta*.

The oil of *athamanta oreoselinum* is obtained by distillation of the plant; odor, like juniper; with hydrochloric acid it gives a fluid compound  $C_{20}H_{16} + HCl$ .

*Gaultherilen* occurs, in common with salicylate of methyl, in the oil of *Gaultheria procumbens* (see page 218).

*Imperatoria oil* occurs in the root of *imperatoria ostruthium*.

*Galanga oil* (Galgantöl) is contained in the root of *galanga minor*.

*Cascarilla Oil.* The crude oil is a mixture of at least two oils, which also contain oxygen.

*Lavender oil, spikenard oil, rosemary oil, oil of Mentha viridis, and Origanum vulgare,* are mixtures of the terebenes with oxygenous oils, probably common camphor.

*Caoutchin* (Caoutchissine: Kautschin, G.):  $C_{20}H_{16}$ .

Amongst the oils obtained by the dry distillation of caoutchouc, one is found which, by fractional distillation, goes over at  $140$  to  $200^\circ$ , and from which, by repeated distillation with water, an oil is obtained, whose boiling point is constantly at  $171^\circ$ ; it possesses an agreeable odor, like lemon oil; behaves in its relations quite like oil of turpentine, and produces with hydrochloric acid, a fluid compound which consists of  $C_{20}H_{16} + HCl$ .

*Amber Oil.* Also from the empyreumatic oils, obtained by the



dry distillation of amber, by fractional distillation an oil may be separated which boils at  $170^{\circ}$ , and consists of  $C_{20}H_{16}$ . If this oil be warmed with dilute nitric acid, we obtain, with evolution of nitrous acid, a yellow mass of resin of musky odor, called *artificial musk*, said to consist of  $C_{15}H_8NO_7$ .

*Petrolen*:  $C_{20}H_{16}$ , occurs in various so-called bitumens in combination with asphaltum, and is obtained by distilling these bitumens with water; pale-yellow, odor peculiar; boiling point  $280^{\circ}$ , probably consists of  $C_{40}H_{32}$ . Petrolen.

*Oil of wine* (light?), which is obtained by the decomposition of ether-sulphate of elayl, is believed also to consist of  $C_{20}H_{16}$  (see page 128).

*Volatile Oils, which do not belong to the Terebenes.*

As the terebenes correspond to the formula  $C_{10}H_8$ , so valerian oil, sage oil, and wormseed oil, may be considered as oxides of a radical  $=C_{12}H_{10}$ , and  $C_{18}H_{15}=2C_6H_5$  and  $3C_6H_5$ .

*Valerol*:  $C_{12}H_{10}O_2$ , is the oxygenous oil of valerian oil; crystallizes a few degrees below  $0^{\circ}$  in colorless, transparent prisms, which fuse at  $20^{\circ}$ . In the air, it is converted gradually into valerianic acid. Valerol.

*Sage oil* occurs in *Salvia officinalis*, and, when old, is always a mixture of  $C_{12}H_{10}O$  with  $C_{18}H_{15}O_2$ . Sage oil.

*Wormseed Oil*:  $C_{18}H_{15}O_2$ , is obtained by distilling with water the so-called worm-seed (*Semen-cynæ*). Worm-seed oil.

*Thuja Oil*. The oil obtained by distillation of the young twigs of *Thuja occidentalis*, is a mixture of at least two oxygenous oils. When freshly prepared, it is completely colorless; smells like thuja, and tastes sharp. Thuja oil.

*Cedar Oil*:  $C_{32}H_{26}$ , and *Cedar Camphor*:  $C_{32}H_{28}O_2$ . The crude cedar oil occurring in commerce, is a mixture of a fluid oil, and a solid camphor. If the crude oil, which appears as a soft crystalline mass, be strongly expressed, and the fluid part distilled with water, we obtain the cedar oil pure. Odor agreeable; sp. gr. 0.98; boiling point  $239$  to  $248^{\circ}$ . Cedar camphor, which remains after expression, is repeatedly crystallized from alcohol; a beautiful, shining, crystalline mass of aromatic odor; fuses at  $74^{\circ}$ ; boils at  $282^{\circ}$ . When distilled with anhydrous phosphoric acid it gives fluid cedar oil. Cedar oil and cedar camphor.

*Menthen* (Peppermint Oil):  $C_{20}H_{18}$ , and *Menthen-camphor*:  $C_{20}H_{20}O_2$ . We obtain menthen, when menthen camphor (solid peppermint oil) is distilled with anhydrous phosphoric acid. A clear, transparent, mobile fluid; of pleasant, peculiar odor, and cooling taste; sp. gr. 0.851; boils at  $163^{\circ}$ . *Menthen camphor* is separated in the cold from oil of peppermint (procured from *Mentha piperita*, Menthen and menthen camphor.



in colorless prisms, which possess the smell and taste of peppermint; fuses at  $34^{\circ}$ ; boils at  $213^{\circ}$ . The *fluid part* of *peppermint oil* is colorless, and possesses a penetrating, cooling taste.

*Monarda Oil*:  $C_{30}H_{21}O(?)$ , and *Monarda Camphor*:  $C_{20}H_{14}O_2$ .

Monarda oil.

Monarda camphor.

The crude monarda oil procured from *monarda punctata*, is a mixture of fluid oil and camphor. The fluid oil has a yellowish-red color, and an odor like thyme. The camphor crystallizes in shining crystals; odor like thyme; fuses at  $48^{\circ}$ ; is easily soluble in alcohol and ether, and may be distilled with water.

Nutmeg-flower oil.

*Nutmeg-flower Oil*:  $C_{16}H_{16}O_5$ , is separated from nutmeg-blossom oil (*Oleum macidis*) in brittle, hemispherically grouped crystals; possesses the odor of the oil; fuses above  $100^{\circ}$ ; easily dissolves in boiling water, alcohol, ether, potash-lye, and nitric acid.

Marjorana camphor.

*Marjorana Camphor*:  $C_{14}H_{15}O_5(?)$ , is separated from marjorana oil, in white, hard crystals; heavier than water; behaves to boiling water, etc., like the preceding compound.

Sassafras camphor.

*Sassafras Camphor*:  $C_{20}H_{10}O_4$ . From the crude sassafras oil (obtained from the root of *Persea* or *Laurus sassafras*) are deposited, after considerable time, colorless, transparent, four-sided prisms, in clusters, possessing the smell and taste of the fluid oil; at  $7^{\circ}.5$  fuses and stiffens to a crystalline mass. Slightly soluble in water, easily soluble in anhydrous alcohol. If ammonia gas be conducted into distilled sassafras oil, accompanied by great refrigeration, large crystals are deposited. With *bromine* it gives a compound which crystallizes in white needles, and consists of  $C_{20}H_2Br_8O_4$ .

Rose oil and rose camphor.

*Rose Oil*. The oil of roses, obtained by distilling *Rosa sempervirens* and *centifolia* with water, is distinguished for its remarkable rose-odor; it is not easily soluble in alcohol, and shows a mixture of fluid oils of peculiar odor, and one *solid*, inodorous, which consist of  $C_{16}H_{16}$ . The last-mentioned oil is completely white at  $25^{\circ}$ ; butter-like; fuses at  $75^{\circ}$ , and boils at  $280$  to  $300^{\circ}$ ; burns with a clear flame.

Violet camphor.

*Violet Camphor* (Irin). If the roots of *iris florentina* be distilled with water, after a short time crystals are deposited from the distillate, which possess an agreeable violet-odor.

Helenium camphor.

*Helenium Camphor* (Helenin, Inuline):  $C_{21}H_{14}O_3(?)$ . It is found in the roots of elecampane (*Inula helenium*), and can be procured by distillation with water, as well as by extraction with alcohol. White four-sided crystals; insoluble in water, easily soluble in alcohol and ether; fuses at  $72^{\circ}$ ; boils at  $275^{\circ}$ . If helenin be slowly fused, it stiffens, in cooling, to a crystalline mass, but if it be for some time retained in a

fused condition, it no longer shows, after stiffening, a crystalline structure. Caustic alkalies and acetic acid dissolve without decomposing it. If helenium-camphor be distilled with *anhydrous, phosphoric acid*, we obtain a light colorless fluid—*helenen*:  $C_{19}H_{13}$  (?). The camphor, when treated with *nitric acid*, gives a *nitro-combination*  $C_{21}H_{13}NO_4O_3$ , and with *chlorine* a chlor-combination  $C_{21}H_{13}ClO_3 + HCl$ (?).

*Asarum Camphor* (Asarin, Asarone):  $C_{20}H_{13}O_5$ .  
 Upon the aqueous distillate of the root of *Asarum europeum* swims an oil, which soon becomes solid, and crystallizes. If these crystals be dissolved in alcohol, and the solution mixed with water, there are deposited small needles of *asarit*, of silky lustre; an oily mass settles to the bottom, which mass, after some time, becomes solid; it is a mixture of camphor and oil, which are mechanically separated. The camphor forms white transparent crystals; fuses at  $40^\circ$ , boils at  $280^\circ$ , and suffers by distillation a partial decomposition. If the alcoholic solution be boiled longer, the camphor is converted into a red, resinous, amorphous mass. *Chlorine* decomposes the camphor, forming a combination  $= C_{20}H_{11}Cl_2O_5$ .  
 Asarum camphor.  
 Asarit.

*Anemonin* (Pulsatillen Camphor, Anemone Camphor):  $C_{15}H_6O_6$ , is deposited from the aqueous distillate, which is obtained by distilling the plants—*Anemone pulsatilla*, *pratensis*, and *nemorosa*; forms acicular crystals, which are easily soluble in boiling alcohol, not easily in cold; easily pulverized, tasteless at first, but after a short time a highly burning sensation, and numbness of the tongue commences; it is, at first, soft at  $150^\circ$ , and decomposes at a high temperature. Anemonin completely saturates pure alkalies; but acids precipitate no anemonin, yet they precipitate a yellow gummy mass; easily soluble in water.  
 Anemonin.

If *anemonin* be boiled with baryta water, it is converted into *anemoninic acid*  $C_9H_4O_4$ . Sometimes  
 Anemoninic acid.  
 there is deposited from the distilled water of *Anemone nemorosa* another white acid-reacting body in the form of a light, voluminous, volatile powder, called *anemonic acid*, consisting of  $C_{15}H_7O_7$ .

*Nicotianin* (Tobacco Camphor). If tobacco-leaves be distilled with little water, a small portion of a fatty substance goes over, which has the odor of tobacco, and an aromatic bitter taste; insoluble in water and cold alcohol, but soluble in boiling alcohol, ether, and fatty oils.  
 Nicotianin.

*Cantharides Camphor* (Cantharidin):  $C_{10}H_6O_4$ .  
 Spanish flies (*Lytta vesicatoria*, *vittata*, etc.) are digested with water, and the aqueous extract, after evaporation, is digested with hot strong alcohol. The alcoholic solution is evaporated, the residue treated with ether, from the etheric fluid by spontaneous evaporation, the cantharadin is obtained in small, colorless, mica-like crystals, which fuse easily, and sublime un-  
 Cantharides camphor.

changed. Insoluble in water and cold alcohol, soluble in boiling alcohol, in ether, and the fatty oils; reacts neutral; brought in small quantity upon the skin, produces blisters.

**Ferment oils.** *Ferment Oils.* By the digestion of *Gentiana centaureum*, of the leaves of *Quercus robur*, *Millefolium*, *Echium vulgare*, etc., with water, oily compounds, which are obtained by distillation, are formed in small quantity, and are called ferment oils.

*Apple Oil* is obtained, when certain apples (Reinette und Calvilläpfel) are distilled with water. If the oil-cakes, which remain after the expression of the oil of almonds, nuts, etc., be distilled with water, after fermentation has commenced, a volatile oil is obtained, which is called *Cyano oil*; it is colorless, volatile, and has a penetrating smell like that of bitter almonds.

### THE RESINS.

**Occurrence of resins.** The resins are among the most extensively diffused compounds of the vegetable kingdom, and a plant can scarcely be found, in which a substance does not occur belonging to the resins. Also in nature are found several fossil substances, whose origin may be traced to the vegetation of a former period, and which, in relation to properties and constitution, agree with the resins, and are named fossil resins, as amber, berengelite, etc.; by dry distillation of organic substances arise the so-called pyro-resins. In general, we class among the resins all substances which are solid at ordinary temperatures; fuse by heat; do not volatilize unchanged; become negatively electric by rubbing; are insoluble in water, dissolve in alcohol, partly in ether and oil of turpentine; melt together with fats; appear mostly inodorous, etc. Many substances, which, indeed, show this behavior, cannot, on account of their chemical relations, be here classed, particularly a large series of coloring matters, and a few indifferent compounds, as, in general, the idea of resin is very vague. Most resins are produced, without doubt, by the action of the oxygen of the air upon volatile oils (*vide p.* 256).

**Production of resins.** *Production of Resin.*—In many plants, as in all species of *Pinus*, in the different species of the genus *Copaifera*, is found a solution of resins in volatile oils, so abundant that it flows out in a great quantity, partly from accidentally arising openings, and partly from incisions intentionally made. Such mixtures are properly called balsams. If these balsams remain a long time exposed to the air, the oil, in part volatilizes, and is partly converted into resin, and if such balsams are distilled with water, the volatile oil passes over with the aqueous vapor, whilst the resin remains behind, and, by continued boiling with water, may be freed from the adhering oil.



If the resin does not readily flow out, the plants, or parts of plants, are dried, and digested with alcohol. The alcoholic extract, after the separation of the fat and wax-like substances, is mixed with water, the alcohol is distilled off, and the resin, which is insoluble in water, and therefore separates, after requisite washing, is freed from the adhering water by long continuance upon the water-bath. The *milky juices*, which occur in particular vessels of many plants, are mostly intimate mixtures of resin, gum, etheric oils, and water; by drying these mixtures, we obtain the so-called *gum-resins*, as galbanum, ammonia-resin, assafetida, and sagapenum. If these are intimately mixed with water, we obtain emulsions; by alcohol, the resins of the gum-resins can be withdrawn.

*Resins are mostly Mixtures.*—Since most resins are produced by oxidation of volatile oils, and since the latter, as obtained by distillation of plants with water, generally consist of several oils, so must the resins which these produce be mixtures of different resins; therefore, by different treatment with alcohol, ether, petroleum, oil of turpentine, etc., they can be separated into different resins. Many resins give compounds with potassa, soluble in alcohol; others insoluble ones; and a third class behaves indifferently; not combining with potassa.

The resins are mixtures.

*Properties of Resins.*—Many resins crystallize from their alcoholic solution, others, on the contrary, appear as transparent masses, mostly yellow. In their pure state, they are inodorous, brittle, and easily pulverized; but if they still contain oil, they appear soft, and possess the odor of the oils (hard resins and soft resins). A few resins are only soluble in boiling alcohol, and are completely deposited after the cooling. Ether dissolves many resins, but not all. Resins soften in hot water, then are kneadable, and may be drawn into slender threads; their specific gravity varies from 0.92 to 1.2; they are easily inflammable, and burn with a clear sooty flame.

Properties of resins.

*Constitution of Resins and their Compounds.*—Many resins possess distinct acid properties. Their alcoholic solutions react acid, and drive by boiling carbonic acid from the carbonates of the alkalis; they agree in this view with the higher members of the fat acids, and are to be considered as real acids. From the saturating capacity of the acid resins, it follows that a large series of them contain 40 atoms C, 30, 28, 27 atoms, and 3, 4, and more atoms O; it may be said that these arise collectively from the terebenes. The acid properties of the resins are the more distinct, as the latter contain more atoms of oxygen. The acid resins easily dissolve in alkali-lyes (resin-soaps), and their alcoholic solutions are not precipitated by addition of

Constitution of resins.



ammonia. On the contrary, there is a class of resins which behave indifferently towards bases, and these have to 40 atoms carbon mostly only 1 atom oxygen; they are not soluble in caustic alkalies, which, however, is sometimes the case if they, in common with acid resins, are treated with concentrated solution of potassa; but they are precipitated if the solution be diluted with water. The acid resins are divided into the feebly acid, the moderately strong, and the strongly acid; the first are insoluble in ammonia and carbonate of potassa; soluble, on the contrary, in pure potassa; the moderately strong dissolve in ammonia, but if the solution be boiled, the ammonia escapes, and the resin is precipitated; finally, the strongly acid can be boiled in a solution of ammonia without precipitation, and, after evaporation, acid compounds remain.

*Use of resins.* *Use of Resins.*—Many resins, especially the so-called gum-resins, are employed in the healing art. They are extensively used as varnish. According to the means of solution, we distinguish *alcoholic*, *turpentinic*, and *oil varnish*. The resins particularly employed for the production of varnish, are *colophonium*, *dammara-resin*, *copal*, *mastich*, *shellac*, *amber*, *sandarac*, etc.

#### SILVIC, PINIC, and PIMARIC ACID:



Colophon.

*Silvic Acid* (Colophon) is found in combination with turpentine oil in turpentine. If the last be distilled with water, the colophon remains behind, and is freed from the adhering oil by boiling with water (if turpentine dries spontaneously in the air, we obtain a pasty mass, the so-named *Resina alba*; if this be repeatedly melted, water being added, stirred round, and the water continually evaporated, there remains the so-called pitch). The colophon thus obtained is not pure silvic acid, but a mixture of silvic acid with pinic acid (amorphous silvic acid). If the colophon be extracted with cold alcohol, and the residue dissolved in two parts of boiling alcohol of 70 per cent., the silvic acid is deposited by cooling, and may be purified by repeated crystallization. Crystallizes in leaflets; is easily soluble in anhydrous alcohol and ether, in fatty and volatile oils, in petroleum, etc.; fuses at  $140^\circ$ , and stiffens to a glassy amorphous mass, whose melting point lies between  $90$  and  $110^\circ$ . From the alcoholic solution of the amorphous acids, it is again obtained in crystals. Separates by dry distillation into water, colophon, and tereben(?); with nitric acid it gives terebenic acid.

The *silvates* with alkali bases are obtained, if the etheric solution of the acid be digested with carbonates, and the etheric fluid evaporated. The *potassa compound* is colorless, and soluble in all proportions in water; the acid salts crystallize. If to an alco-

holic solution of potassa, we add in drops an aqueous solution of a salt, of an earth, or heavy metal, a precipitate is produced of silvate of the earth, or metal. The *magnesia salt* is easily soluble in alcohol.

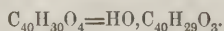
*Pinic Acid* (Amorphous Silvic Acid) possesses Pinic acid.  
not the capability of crystallizing; the *magnesia salt* is said to be insoluble in alcohol. If the pinic acid be melted, it is partly converted into *colopholic acid*, of which the ordinary colophon contains 10 per cent.; it possesses a brown color, and is scarcely soluble in hydrous alcohol.

*Pimaric Acid*. The turpentin, which is obtained in Pimaric acid.  
the sand plains of Bordeaux from the *Pinus maritima*, is converted in the air into a white resinous mass, which occurs in commerce under the name of *gallipot*; it consists mostly of pimaric acid. We procure pimaric acid from colophon of Bordeaux in the same manner as we do the silvic acid from common colophon. It forms crystalline crusts; is easily soluble in ether and boiling alcohol; melts at  $125^{\circ}$ , but is again solid first at  $68^{\circ}$ . By long heating, it is converted into silvic acid. Its salts agree with those of silvic acid. If it be long boiled with *nitric acid*, we obtain *azomarinic acid*,  $2\text{HO} + \text{C}_{20}\text{H}_{14}\text{O}_2\text{NO}_4$ , as a yellow mass; not crystallizable; insoluble in water, but easily soluble in ether and alcohol; it produces soluble salts with potassa, soda, and ammonia.

*Pimaron*:  $\text{C}_{20}\text{H}_{14}\text{O}$ ; *Resinein*:  $\text{C}_{20}\text{H}_{14}\text{O}$ ; *Resinon*:  $\text{C}_{20}\text{H}_{18}\text{O}_2$ , and *Resineon*:  $\text{C}_{30}\text{H}_{23}\text{O}$  (?), are products of the dry distillation of silvic and pimaric acid.

*Dammaric Acid* (Dammara Resin):  $\text{HO}, \text{C}_{40}\text{H}_{29}\text{O}_7$ , Dammaric acid.  
or  $\text{HO}, \text{C}_{45}\text{H}_{35}\text{O}_3$  (?). From the *Dammara australis*, a tree belonging to the family of Coniferae, a resin exudes, which occurs in commerce as dammara resin (turpentine). This is a mixture of dammaric acid, and hydrocarbon; it is amber yellow; easily fusible, and smells like turpentin. The acid dissolves in alcohol and is precipitated by water. If the residue be treated with ether, the *dammaryl* is dissolved, and should consist of  $\text{C}_{45}\text{H}_{36}$ ; it is a white amorphous powder.

## COPAIVIC ACID:



*Copaiva Balsam*, which, in Brazil and the Antilles, flows from incisions made in the *Copaifera officinalis*, *coriacea*, *multijuga*, etc., is, like turpentine, a mixture of oil and resin, which last consists of indifferent resins, and copaivic acid; the latter can be removed by solution in naphtha. Copaivic acid crystallizes in regular, colorless, almost transparent soft crystals, soluble in alcohol, ether, fatty and volatile oils, as well as in carbonic acid. The alcoholic solution of the acid is not precipitated by *potassa* or

soda; by the addition of water, and an excess of alkalies, a soft and salve-like precipitate forms. The combinations with the earths, and metallic oxides, are obtained by double decomposition; in the dry condition, they are pulverizable. The indifferent resin is glimmering, and soluble in ether and absolute alcohol.

*Resin of Peru Balsam:*  $\text{HO}, \text{C}_{40}\text{H}_{27}\text{O}_5$ . From the so-called Peru balsam a crystalline white powder is sometimes deposited, which crystallizes from the alcoholic solution in rhombic pillars; possesses acid properties, readily dissolves in ether; fuses at  $120^\circ$ ; separates, by rapid evaporation of its ethero-alcoholic solution in amorphous powder, which contains 2 atoms of HO. Gives, with potash and soda, soluble salts; from a solution in ammonia, there remains after evaporation, the pure resin. If the resin be treated with dilute nitric acid, we thus obtain an acid  $= \text{C}_{30}\text{H}_9\text{O}_{14}$ , and a light-yellow resin.

*Betula resin.* *Betula Resin* (Birch Resin, Betulin):  $\text{C}_{40}\text{H}_{33}\text{O}_3$ . It is found in the bark of the *Betula alba*. Crystallizes from the alcoholic solution; gives an aromatic odor by heating; fuses at  $200^\circ$ ; is insoluble in water, not easily soluble in alcohol, but easily soluble in ether, oil of turpentine, and oil of almonds.

*Elemi resin.* *Elemi Resin.* Elemi resin, which is obtained from incisions in the *Amyris elemifera* and *Ceylonica*, is a mixed resin. Cold alcohol extracts 60 per cent. of acid resin; if the residue be dissolved in boiling alcohol, there separates, by the cooling, an indifferent resin in crystals, which consists of  $\text{C}_{40}\text{H}_{33}\text{O}$ . If we let the alcoholic solution evaporate, the resin absorbs water, and is partly converted into amorphous resin.

*Anime resin.* *Anime Resin* is obtained from a tree growing in Brazil—the *Hymenæa courbaril*. Consists, like elemi resin, of an indifferent crystallizable resin,  $\text{C}_{40}\text{H}_{33}\text{O}$ ; insoluble in cold alcohol, and an acid resin soluble in cold alcohol.

*Euphorbium.* *Euphorbia Resin* is obtained by incision in several species of *euphorbia*. It appears in irregular yellowish bodies; inodorous, and of extremely sharp burning taste, and possesses the property of drawing blisters. Consists of several resins, of which one is easily soluble in cold alcohol, another not easily soluble, and a third insoluble; the last crystallizes from the boiling alcoholic solution, possesses a very sharp taste, and should consist of  $\text{C}_{45}\text{H}_{35}\text{O}_4$ .

*Sandarach.* *Sandarach* is procured in warm countries from *Juniperus communis*. Appears in small, pale-yellow, transparent, hard, and brittle corns of bitter, balsamic taste, and of an odor resembling turpentine. Consists of three acid resins of different solubility in alcohol. The one easily soluble in cold alcohol, consists of  $\text{C}_{40}\text{H}_{31}\text{O}_6$ ; that not easily soluble, of  $\text{C}_{40}\text{H}_{31}\text{O}_5$ , and that soluble in boiling alcohol of  $\text{C}_{40}\text{H}_{30}\text{O}_6$ .



*Olibanum* must be derived from an *amyris*; a *Olibanum*. beautiful sort comes from the *Boswellia serrata*.

Appears in yellow kernels; is soft by chewing; of aromatic and somewhat sharp taste; is a mixture of at least two resins, of which one is said to consist of  $C_{40}H_{32}O_4$ .

*Mastich* is obtained upon the island of Chios, by *Mastich*. incisions in the *Pistacia lentiscus*. Appears in yellowish semi-transparent kernels; softens between the teeth; possesses a feebly aromatic taste, and diffuses, when thrown upon glowing coal, an odor not disagreeable; decomposes at  $120^\circ$ . Consists of a resin  $C_{40}H_{31}O_4$ , easily soluble in alcohol; and one  $C_{40}H_{31}O_2$ , soluble with difficulty in the same; the latter may be drawn into long threads.

*Copal* flows spontaneously from the *Hymenæa* *Copal*. *verrucosa*, and comes from Calcutta, Bombay, and Madagascar. Occurs in yellow, hard, tasteless, inodorous, transparent pieces, often inclosing insects. By heating, becomes soft and elastic; melts and decomposes, accompanied by diffusion of an aromatic odor. In the air, copal absorbs oxygen, producing acid resins, which are as easily soluble as the original in alcohol and turpentine oil. India copal is a mixture of fine resins; if it be brought together with alcohol of 65 per cent., one part is dissolved, and the residue may again be divided into two parts by anhydrous alcohol. If an alcoholic solution of copal be mixed with an alcoholic solution of acetate of copper, a precipitate is formed, which consists of oxide of copper, and two resins, one of which is soluble in ether; this resin consists of  $C_{40}H_{32}O_5$ ; it resembles the Burgundy pitch; melts at  $100^\circ$ ; dissolves in alcohol of 72 per cent., in ether, and turpentine oil. If the alcoholic solution, separated from the precipitate, be decomposed by an acid, there remains, after evaporation, a resin, which is easily pulverized; soluble in all proportions in alcohol and ether, and consists of  $C_{40}H_{31}O_3$ .

*Amber*. A fossil resin found in the fossil coal-beds *Amber*. of Greenland, East Prussia, France, etc.; the greatest quantity is obtained on the coast of the Baltic, particularly between Kingsberg and Memel. It is probable that amber, like turpentine, is originally exuded from trees. In it we often find impressions of twigs and bark, and it often contains many insects inclosed, of species which no longer appear to be living. Amber occurs in hard-brittle pieces of different sizes, partly colorless, partly light or dark yellow, transparent or opaque, and of a conchoidal fracture and shining smooth surface resembling copal; it is tasteless and inodorous, but diffuses by melting an agreeable aromatic odor. Amber fuses at  $287^\circ$ ; it is, however, decomposed whilst water, petroleum, and succinic acid escape. *Nitric acid* converts it into a yellow resinous mass of musk-like odor, simulta-



neously producing some laurel camphor. Amber is found constituted of  $C_{40}H_{32}O_4$ ; it is, however, a mixture of different substances, and consists of a volatile oil, two resins soluble in alcohol and ether, succinic acid, and a substance entirely insoluble, and named *amber bitumen*.

**Asphalt.** *Asphalt* (Jews-pitch) is often found swimming upon the Dead Sea, and arises apparently by oxidation of petroleum (naphtha); possesses a conchoidal fracture, strong lustre, and resembles obsidian. Many kinds of bitumen, e. g. that from Bechelbronne, Seyssel, and Lobsann, are mixtures of asphalt and petroleum (p. 265.) Is employed as plaster of floors, walks, etc.

**Gum-lac.** *Gum-lac.* From many India trees, for instance, *Ficus religiosa* and *indica*, from *Croton lacciferum*, a juice flows in consequence of punctures which the female of the lac insect (*Coccus lacca*) makes in the bark and twigs. This juice entraps the insect, dries upon the bark, and is called stick-lac. It contains a red coloring matter, which can be absorbed by a weak alkali solution (seed-lac). If stick-lac or seed-lac be boiled out with water, then melted, strained through linen and poured upon a stone plate, we thus obtain the so-named shell-lac. Gum-lac melts by heat, and dissolves in strong alcohol in all proportions, and is also easily soluble in hydrochloric and acetic acid. It possesses the property of an acid, and with an alkali solution gives a solution no longer reacting basic, and which dries to a red brown mass, easily soluble in water and alcohol, and possesses a bitter balsamic taste. It is a mixture of different resins with wax, coloring matter, oleic and margaric acid, etc. Serves for varnish, cement for stone and porcelain, and particularly for sealingwax.

**Benzoin resin.** *Benzoin Resin* is procured from incisions made in the trunk and branches of a tree, the *Styrax benzoin*, growing in Sumatra. Occurs in large brittle lumps, possesses an agreeable odor resembling vanilla, melts at  $95^{\circ}$  under sublimation of benzoic acid; soluble in ether and alcohol; sp. gr. 1.230. Is a mixture of different resins corresponding to  $C_{30}H_{20}O_5$ ,  $C_{70}H_{42}O_{14}$ ,  $C_{40}H_{22}O_9$ .

**Guaiac resin.** *Guaiac Resin* flows from incisions in a tree, *Guaiacum officinale*, occurring in Jamaica and other West India Islands. Comes in large, hard, irregular, transparent masses, outwardly of a brownish-green color and shining fracture, of at first sweetish and later a bitter burning taste and aromatic odor. Completely soluble in alcohol, little soluble in turpentine oil. In the air, as well as by oxidizing action, the resin takes a green color. The alcoholic solution at last assumes a beautiful blue. If the guaiac resin be brought together with different vegetable and animal substances, e. g. with meal, it assumes a blue color. It is a mixture of resin (80 p. c.), gum, extractive matter, guaiac acid, etc.

*Resin* from *Xanthorrhœa hastilis* comes from Australia, and appears in large, dark-yellow pieces of agreeable balsamic odor. Gives by dry distillation, phenole, benzoic, and cinnamic acid. Treated with moderately strong nitric acid, we obtain pikrin-nitric and nitro-benzoic acid; and by distillation with peroxide of manganese and sulphuric acid we procure oil of bitter almonds.

To the most important *Gum-resins* belong Gum-resins.

*Ammonia Gum.* This is said to flow from the root of the *Heracleum gummiferum*. Yellow kernels, of disagreeable odor and astringent sharp taste; consists of 72 p. c. of resin, 22 p. c. gum, volatile oil, etc. *Galbanum* comes from *Bubon galbanum*. *Bdellium* is derived from an unknown tree in the Levant; possesses a disagreeable odor, and a taste resembling turpentine. *Sagapenum* comes from Egypt, from *Ferula persica*; possesses a disagreeable odor, gives by distillation with water an oil smelling like garlic, and containing 50 p. c. resin, 32 p. c. gum, scum, etc. *Assafetida* is procured by incisions in the root of the *Ferula assafetida*. Occurs in reddish, highly disagreeable smelling and tasting masses, and consists of resin, gum, sulphurous oil, (v. 171) etc. *Opoponax* originates from *Pastinaca opoponax*, a tree growing in the East, in Sicily, and Italy; taste sharp and bitter, and possesses an aromatic odor. *Myrrh* comes from the *Balsamodendron myrrha*, a tree growing in Arabia and Abyssinia. Appears in heavy red-brown pieces, easily pulverizable, of peculiar, not disagreeable odor, and bitter warming taste; consists of resin, gum, and ethereal oil of strong balsamic odor. *Ladanum* springs from *Cistus creticus*, a plant growing in Smyrna and Candia. *Scammonium* from Aleppo comes from *Convolvulus scammonia*, and that from Smyrna is from *Periploca secamone*; possesses a strong odor and disgusting taste.

*Gamboge* (*Gummi gutta*). This gum resin, known Gambogia. as a painter's color, comes from East India, from the Islands of Ceylon and Cambodia; is obtained by incisions in the bark of *Stalagmites cambogioides*. Appears in large, round pieces, pulverizable, inodorous, sharp tasting, poisonous; gives, with water, a beautiful yellow emulsion; the alcoholic solution has a red color; consists of 19 p. c. gum and 80 p. c. resin, which is soluble in ether. This resin is hard, easily pulverizable, of yellow color, tasteless, and inodorous; combines with bases, and consists of  $C_{60}H_{35}O_{12}$  (?)

*Dragon's Blood.* This resinous substance is mentioned among the coloring matters.

*Resin of the Cow-Tree* (S. America). The milky juice of the cow-tree (which probably is to be classed as a species of *Brosimum*), which flows abundantly from wounds in the tree, consists of vegetable albumen, wax, and resin =  $C_{35}H_{29}O_2$ , gum, sugar, and water, and often still another body resembling caoutchouc.

*Caoutchouc, Gutta-Percha, and Viscin.*

Caoutchouc.

*Caoutchouc* (Indian-Rubber, Gum-Elastic). A peculiar substance is obtained from many vegetable milky juices, especially from the family of the *Urticaceæ*, the *Euphorbiaceæ*, and *Apocynaceæ*, which, in some respects, belong to the resins, but in others differ very widely from them, and which are called caoutchouc. If this juice, which is a mechanical mixture of caoutchouc, vegetable albumen, water, etc., be presented to the air in thin layers, it thus hardens soon and is converted into a pasty, elastic, brown-yellow mass, which is the ordinary caoutchouc. To obtain the pure caoutchouc from the juice, the latter is intimately mixed with four times its weight of water, and the mixture, left twenty-four hours in a high vessel, may be drawn below by a stopcock. During this time, the caoutchouc collects, cream-like, upon the surface, whilst the other substances remain dissolved in water. The same operation must be several times repeated. The caoutchouc cream is now further freed from the adhering water by gently warming, or by porous substances; in proportion as the water escapes, the mass becomes pasty, and can at last be completely freed from water by pressing. If it once become coherent, it can in no way be again diffused in water. It is now white, almost transparent, in thin layers, completely elastic, has no trace of fibrous texture, and adheres feebly, on standing, to whatever touches its surface. If you cut the caoutchouc with clean, sharp shears, the separated edges readily adhere to each other (caoutchouc tubes). In the cold it is solid and little limber, a non-conductor of electricity, quite insoluble in alcohol and water, but dissolves in anhydrous ether, and remains, after evaporation, again elastic; in the same manner it dissolves without losing its elasticity, in turpentine oil, lavender oil, and particularly in the empyreumatic oils, which are obtained by the dry distillation of caoutchouc. It melts at  $200^{\circ}$ , but forms, after cooling, an adhesive semi-fluid mass, no longer becoming solid; strongly heated it inflames and burns with a sooty flame. By dry distillation it produces different hydrocarbons of varying volatility, as caoutcheen, heveen (boils at  $315^{\circ}$ ), caoutchin (p. 264), etc. Pure caoutchouc, consists of  $C_8H_7$ . In the arts, caoutchouc has manifold uses; on account of its unchangeability by chlorine, bromine, acids, and alkalies, it is much employed by chemists as a means of binding together glass tubes; it is also used for surgical instruments, to produce water-tight materials, shoes, etc.

Gutta-percha.

*Gutta-percha*. This substance comes from the East Indies, and is a dried milky juice of a *Bassia*, from the family of the *Sapotææ*. This body agrees in its essential properties with caoutchouc. At ordinary temperatures it is solid,



hard, and scarcely elastic. But if it be put into hot water, it becomes completely elastic; its best solvent is turpentine oil. Gutta-percha is extensively used at present similarly to caoutchouc, to which, in many respects, it is preferred. It has the same constitution as caoutchouc, and is to be considered a modification of that substance.

*Viscin* (Birdlime) is found in the berries of the *Viscin*. mistletoe, and probably, also, in the green twigs of *Ficus elastica*. A water-clear, adhesive substance, insoluble in water and alcohol, but soluble in ether, volatile oils, and warm potash solution; serves for the production of birdlime, which is obtained by expressing the mistletoe berry; by mixing the expressed juice with water the viscin is separated. It is said to contain 15 p. c. of oxygen.

## APPENDIX TO THE RESINS.

*Lichenstearic Acid*:  $\text{HO}, \text{C}_{28}\text{H}_{53}\text{O}_3$ , is found in *Lichenstearic acid*. Iceland moss (*Cetraria islandica*). If the lichen be boiled with alcohol and some carbonate of potassa, then filtered and the fluid diluted with much water, thus, by the addition of hydrochloric acid, a copious precipitate is formed, which consists of a green coloring matter—cetrarin, a nitrogenous substance, and lichenstearic acid. If we boil this precipitate with alcohol of 42 per cent., the lichenstearic acid is dissolved; the latter is obtained by repeated crystallization from the aqueous alcohol. It appears as a white porous mass, consisting of small needles of mother-of-pearl lustre; inodorous, and of a rancid, bitter taste. Insoluble in water; easily soluble in alcohol, ether, fatty and volatile oils; melts at  $120^\circ$ ; stiffens crystalline; with alkalies gives easily soluble salts, which foam by boiling like soap and water.

*Anacardic Acid*:  $2\text{HO}, \text{C}_{44}\text{H}_{90}\text{O}_5$ . If the nut- *Anacardic acid*. like fruit of *Anacardium occidentale* (the cashew-nut, West India) be extracted with ether, there remains, after evaporating the etheric solution, a red-brown, almost odorless liquid, which consists of anacardic acid and anacardium oil. If this mixture in alcoholic solution be digested with freshly precipitated hydrate of lead, we have anacardate of lead precipitated, whilst the anacardium oil remains dissolved. The lead compound is treated with sulphide of ammonium, and from the solution of the ammonia salt, the anacardic acid is procured by precipitation with hydrochloric acid. In the pure state, the acid appears a white, crystalline, inodorous mass, of slightly aromatic and afterwards burning taste; melts at  $26^\circ$ ; non-volatile; makes upon paper a grease-spot, and then smells like rancid fat. Gives, with bases, neutral



and acid salts; the former contain 2 atoms base, the latter 1 atom of base, and still another atom of water; they are partly crystalline, and partly amorphous. The *potassa salt* dissolves in water like a soap, and is again precipitated from the solution by common salt.

*Anacardium Oil*:  $C_{42}H_{31}O_4$ , appears as a yellow fluid; of rather agreeable odor, when warmed; insoluble in water, easily soluble in alcohol and ether; non-volatile; combustible; sp. gr. 0.978 at  $23^\circ$ ; slowly oxidizes in the air. With vinegar of lead and cardium oil forms a white precipitate; soluble in alcohol; becoming brown in the air, and which consists of  $PbO, AcO_3 + 3PbO, C_{42}H_{31}O_4$ . If we put anacardium oil upon the skin, and cover the place with filter paper, after 3 to 7 minutes a violent burning commences, and in from 6 to 8 hours a blister is produced.

*Lithofellinic acid*. *Lithofellinic Acid*:  $HO, C_{40}H_{36}O_7$ . This acid forms the principal constituent of the so-called oriental *benzoare*; is also sometimes found in gall-stones. We dissolve the benzoare in potassa solution, and precipitate by hydrochloric acid. The precipitated lithofellinic acid is obtained by solution in boiling alcohol and recrystallization. Forms microscopic six-sided prisms; easily pulverizable; insoluble in water, soluble in alcohol; melts at  $204^\circ$ , and stiffens to a resinous mass, which is strongly electric by rubbing, and melts at  $110^\circ$ . From the alcoholic solution we obtain the fused acid again in crystals. Sublimes in a current of air; gives, by distillation, water and pyro-lithofellinic acid, and, with nitric acid, the nitro-lithofellinic acid. Forms with the alkalies soluble salts, with the oxides of the heavy metals insoluble ones.

*Cholalic acid*. *Cholalic Acid*:  $HO, C_{48}H_{39}O_9$ . This acid is obtained, if cholinic acid (*vide* Glycocoll, p. 347) be boiled with acids or alkalies. The cholinic acid separates into cholalic acid and glycocoll. The cholalic acid is precipitated by hydrochloric acid, and is made pure by recrystallization from alcohol and ether. Crystallizes from the etheric solution in direct columns; unaffected by the air; insoluble in water, and easily soluble in alcohol; tastes bitter-sweet like gall; is easily soluble in alkalies, and is precipitated from the solution by acids, as a soft, resinous mass, which, after a little time, unites to form a cluster of crystals. The *potassa salt* separates from the alcoholic solution in crystals; by slow evaporation it forms a varnish; is insoluble in excess of potash-lye. If we mix the solution of the neutral potassa salt with chloride of calcium, thus is formed a thick pasty precipitate, which, by the addition of a few drops of ether, is converted into crystals, which consist of  $CaO, C_{40}H_{39}O_9$ . If to a solution of cholalic acid salts a solution of sugar be added, and then gradually also sulphuric acid, there is formed a beautiful purple-colored solution.

*Choloidic Acid*:  $C_{48}H_{39}O_9$ . This resinous acid is Choloidic acid. obtained if cholalic acid be heated to  $195^\circ$ ; or if it be boiled a long time with concentrated hydrochloric acid. It appears as a white, amorphous, resinous mass; easily pulverizable; insoluble in water, easily soluble in alcohol; becomes soft by warming; melts at  $150^\circ$ , and is converted at  $295^\circ$  into dyslysin under the loss of water. A very weak acid; gives, with the alkalis, pure, bitter-tasting salts, which are decomposed even in the cold by carbonic acid. The alkali salts appear as gum-like masses, soluble in water and alcohol; the combinations with the earths and with oxides of heavy metals are insoluble.

*Dyslysin*.  $C_{48}H_{36}O_6$ . If choloidic acid be a still Dyslysin. longer time boiled with hydrochloric acid, it gradually loses its solubility in alcohol as well as its fusibility. If the obtained mass be extracted with water and alcohol, then dissolved in ether and the solution mixed with alcohol, the dyslysin falls as a gray-white mass. Insoluble in water, cold alcohol, alkalies, and acids, but soluble in boiling alcohol. If it be boiled with an alcoholic potassa solution, it is dissolved and converted into choloidic acid.

According to other statements, choloidic acid is a mixture of *cholinic* and *fellinic acid*, which can be separated by evaporation of the ammonia salt. Choline of ammonia separates at first in the state of a white, soap-like mass, whilst the fellinate of ammonia is obtained as a brownish, greasy mass. By *cholanic acid*, we understand a kindred acid, said to be obtained from putrid gall.

*Nitracol*. If we distil choloidic acid with nitric Nitracol. acid until red vapor is no longer evolved, we thus obtain a distillate which, after repeated distillation with water, contains an oily body (nitracol, v. p. 154), together with acetic, capronic, and capric acid, etc. Cholesteric and oxalic acid remain as residue. Nitracol is colorless, heavier than water, smells stinging and benumbing, excites to tears, reddens litmus, is little soluble in water, but easily soluble in alcohol. If nitracol be heated with water, to  $100^\circ$ , it separates into nitrous acid and *cho-* Cholacrol. *lacrol*, which exhibits a pale-yellow, heavy, hot-smelling oil. It consists of  $N_2C_8H_5O_{13}=C_8H_5O_5 \cdot 2NO_4$ . If nitracol be left a few days in contact with cold dilute potash solution, thus are obtained crystals of *nitracolate* of *potassa*  $= KO, C_2HO, 2NO_4$ .

*Cholesterin* (Gall Fat):  $C_{81}H_{69}O_3 + 2HO$ , is the Cholesterin. principal constituent of very many gall-stones; is also found in the gall, in blood, in the brain, and in many pathological secretions. If gall-stones containing cholesterin be boiled out with alcohol, the cholesterin separates by the cooling in white, fatty leaflets, which melt at  $145^\circ$ , stiffen again at  $135^\circ$  and distil at  $360^\circ$ . Insoluble in water, dissolves in nine parts boiling alcohol, and still easier in ether. Pure alkalies do not attack cholest-

terin, but if it be warmed to  $60^{\circ}$ , thus are obtained three hydrocarbons, which are called *cholesterilens*, and correspond to the formulæ  $C_{32}H_{26}$ ,  $C_{22}H_{18}$ , and  $C_{27}H_{22}$ . The compound  $C_{32}H_{26}$  is insoluble in ether, little soluble in alcohol, earthy, amorphous, crystallizes from hot turpentine oil, and melts at  $240^{\circ}$ . The compound  $C_{22}H_{18}$  crystallizes in very shining needles, dissolves in ether but not in alcohol, and fuses at  $255^{\circ}$ . The compound  $C_{27}H_{22}$  is a resinous, amorphous mass, easily soluble in ether but not in alcohol, and melts at  $127^{\circ}$ .

*Cholesteric Acid*:  $C_8H_4O_4$ . If we boil cholesterin a long time with nitric acid, it is converted first into a resinous mass, which, by continued action, is changed into cholesteric acid, under the formation of acetic, butyric, and capronic acid, etc. Cholesteric acid is also procured by the action of nitric acid upon choloidinic acid. It appears as an amorphous, pale-yellow, gum-like mass, which deliquesces, dissolves in alcohol, and forms insoluble compounds with the alkalis and the oxides of the heavy metals. The *silver salt* is soluble in boiling water, and separates crystalline by cooling.

*Ambrain*. *Ambraïn* (ambrein):  $C_{36}H_{33}O$  (?). This body is procured from ambergris in the same manner as cholesterin from gall-stones. Crystallizes in delicate white needles spherically united; possesses an agreeable odor, melts at  $35^{\circ}$ , and sublimates at  $100^{\circ}$ ; insoluble in water, easily soluble in alcohol and ether, and gives, with nitric acid, *ambraic acid*, which must contain nitrogen.

*Castorin*. *Castorin* is found in Castoreum. Crystallizes from the hot alcoholic solution in fine four-sided needles grouped together; of slight odor, and a metallic taste. Easily pulverizable, melts in boiling water but not in cold, easily soluble in ether but not easily in alcohol. Dissolves in boiling acetic acid and in pure alkalis without decomposition. Gives an acid by treatment with nitric acid.

*Cerebric Acid*. *Cerebric Acid* (Brain Fat). A constituent of brain; is white, granular, of crystalline appearance, soluble in boiling alcohol, insoluble in cold ether; in water it swells up like starch. Contains 2 p. c. nitrogen, and 0.9 p. c. phosphorus.

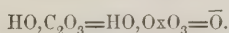
## SECOND DIVISION.

### CARBYLS.

To the class of the Carbyls belongs every radical which consists of two or more atoms of carbon. As yet, but few of these radicals are known, and those only in combination with oxygen. Here belong:—

Oxalic Acid	.	.	.	HO, C <sub>2</sub> O <sub>3</sub> ,
Mesoxalic Acid	.	.	.	HO, C <sub>3</sub> O <sub>4</sub> ,
Millithic	"	.	.	HO, C <sub>4</sub> O <sub>5</sub> ,
Croconic	"	.	.	HO, C <sub>5</sub> O <sub>6</sub> ,
Rhodizonic Acid	.	.	.	HO, C <sub>7</sub> O <sub>7</sub> .

### OXALIC ACID:



The radical of oxalic acid is C<sub>2</sub> and named *Oxatyl*. Oxalic acid is much diffused in the vegetable kingdom; it is found free in the vetch, combined with potash in wood-sorrel (*Oxalis acetosella*) and in *Rumex acetosa*, etc., and as oxalate of lime in very many species of lichen, which often contain one-half their weight of oxalic acid; it is also contained in many urinary calculi. It is formed by the decomposition of most organic compounds by *nitric acid*, *hypermanganic acid*, and *hyperchloric acid*, etc., by the action of hydrate of potash, by increased temperature upon many organic compounds accompanied by evolution of hydrogen (woody fibre, sugar, starch, tartaric acid, succinic acid, etc.; compare further saccharic acid, cyanogen, urea, uric acid, rhodizonic acid, etc.).

From the *oxalic salts* (KO, HO, 2OxO<sub>3</sub>) the oxalic acid is obtained by saturation with carbonate of potassa, precipitation by acetate of lead and decomposition of the oxalate of lead by hydrosulphuric acid or sulphuric acid. By evaporation of the aqueous solution, the oxalic acid is obtained in crystals. *From sugar*—One part sugar dried at 100° is mixed with 8.25 parts nitric acid of 1.38 sp. gr., and the mixture evaporated in a beaker-glass to one-sixth; we obtain of oxalic acid 60 p. c. of the amount of sugar employed. The oxalic acid is purified by recrystallization. Oxalic acid crystallizes from the aqueous solution in long prisms, generally striped,



and containing two atoms of water of crystallization, which water is lost at  $130^{\circ}$ . If the pure hydrate of oxalic acid be cautiously heated to  $150$  or  $160^{\circ}$ , it is completely sublimed, and forms a crystalline acid-tasting mass, mostly hanging together. 100 parts water dissolve 6.9 parts acid at  $10^{\circ}$ ; it is dissolved in every proportion by boiling water, and is also somewhat soluble in alcohol. Oxalic acid is the strongest organic acid; one part of it diffused in 200,000 parts water has still a sour taste; poisonous. If oxalic acid be suddenly heated to  $155^{\circ}$ , it completely decomposes into formic and carbonic acid and carbonic oxide. *Nitric, chloric, and iodic acid, the superoxides, etc.*, oxidize the oxalic acid forming carbonic acid. Heated with *hydrated sulphuric acid*, it separates into equal quantities of carbonic oxide and carbonic acid; moist hydrochloric acid produces the same. Fused with *hydrate of potash*, it decomposes into carbonic acid and formic acid.

*Oxalates.* Oxalic acid rivals in affinity for bases the strongest inorganic acids; it forms basic, neutral, acid, and many double salts. If the salts are heated we obtain, according to the base, a carbonic acid salt under evolution of carbonic oxide, or a mixture of carbonic acid and carbonic oxide, or carbonic acid alone. Most neutral salts, except the alkali, are insoluble in water. Oxalic acid precipitates, in the presence of ammonia, lime and oxide of lead as completely as sulphuric acid does baryta.

The *Neutral Ammonia Salt*:  $\text{NH}_4\text{O}, \text{OxO}_3 + \text{aq}$ , forms shining, tufted crystals, which dissolve in 28 parts cold water. The *acid salt*,  $\text{NH}_4\text{O}, \text{HO}, 2\text{OxO}_3 + 2\text{aq}$ , is a crystalline powder not easily soluble. *Oxamid*,  $\text{NH}_2, \text{OxO}_2$ . The neutral ammonia salt, by heating in a retort, decomposes into ammonia, water, carbonic acid, carbonic oxide, cyanogen, and oxamid. It is most easily obtained by shaking oxalate of ethyl with aqueous ammonia; white, inodorous, tasteless, and indifferent powder, almost insoluble in water and not easily soluble in alcohol and ether; decomposes, by heating in a retort, into cyanogen, ammonia, carbonic acid, etc.; if it be conducted through a glowing tube, we also obtain urea; is again converted, under the co-operation of dilute acids and alkalies, into ammonia and oxalic acid by the decomposition of water. *Oxamid-oxalic acid* (Oxaminic acid) *v.* below.

*Simple oxalate of potash*,  $\text{KO}, \text{OxO}_3 + 2\text{aq}$ ; crystallizes in four and six-sided prisms, soluble in 3 parts cold water. The *biacid potassa salt*,  $\text{KO}, \text{HO}, 2\text{OxO}_3 + 2\text{aq}$ , is found in the juice of *Rumex acetosa*, *Oxalis acetosella*, etc. Forms short crystals of sharply acid-biting taste, unaffected by the air; soluble in 40 parts cold and 6 parts boiling water. The *quadroxalate of potassa*,  $\text{KO}, 3\text{HO} + 4\text{OxO}_3$ , crystallizes in very large four-sided prisms of very sour taste.

*Oxalate of lime*,  $\text{CaO}, \text{OxO}_3 + 2\text{aq}$ , is a powder quite insoluble in water, and becomes electric at  $150^{\circ}$ , gives a double salt with chloride of calcium.

*Oxalate of chromium*,  $\text{Cr}_2\text{O}_3, 3\text{OxO}_3$ , is obtained by dissolving oxide of chromium in aqueous oxalic acid; if the cherry-colored solution be heated to boiling, it becomes green, but in cooling resumes its former color. If we let the solution evaporate of itself, there remains a black, glassy mass, which appears violet-red in thin layers; but if the solution be evaporated by continued boiling, the residue is of a green color; the solution gives with ammonia and lime salts no precipitate; the oxalate of chromium gives with the oxalates of alkalis double salts, which contain to 1 atom of oxalate of chromium 1 or 3 atoms oxalate of the alkalis; the former is garnet red and the latter blue.

*Oxalate of Methyl*:  $\text{MeO}, \text{OxO}_3$ , is obtained when equal portions of wood-spirit, oxalic acid, and sulphuric acid are distilled; or, we distil oxalic acid with wood-spirit, often pouring back the distillate. Salt-like compounds of oxalic acid with organic oxides. It crystallizes in colorless rhombs; melts at  $51^\circ$ ; boils at  $161^\circ$ ; soluble in cold water, alcohol, and ether. By warming the aqueous solution, it separates into wood-spirit and oxalic acid.

*Oxalate of Ethyl*:  $\text{AeO}, \text{OxO}_3$ , is obtained like the former compound. Oil-like, colorless fluid; little soluble in water; easily soluble in alcohol and ether. Brought together with potassium, it gives carbonate of ethyl, besides other products. Boils at  $180^\circ$ .

*Oxalate of Amyl*. Oil-like, strong, bug-like smelling fluid; of 0.85 specific gravity; boils at  $262^\circ$  (?).

*Oxamid-oxalic Acid* (Oxaminic Acid):  $\text{HO}(\text{NH}_2, \text{OxO}_2)\text{OxO}_3$ . If ammonia gas be conducted into an alcoholic solution of oxalate of methyl, ethyl, or of amyl, we thus obtain oxamid-oxalic acid combinations of the oxides mentioned. Oxamid-oxalic acid. If the aqueous solution of the oxamate of ethyl be brought drop-wise together with aqueous ammonia, we obtain oxamate of ammonia. If the warm saturated solution of this salt be mixed with the corresponding quantity of sulphuric acid, in this manner, by sudden cooling, the oxaminic acid is separated as a white crystalline powder. By boiling the aqueous solution, the acid is converted into double oxalate of ammonia. Oxaminic acid is also produced by heating double oxalate of ammonia.

*Oxamate of Methyl* (Oxamethylan) forms, from the hot alcoholic solution, white crystals of mother-of-pearl lustre.

*Oxamate of Ethyl* (Oxamethan) crystallizes in shining fatty leaflets; fuses at  $100^\circ$ ; boils at  $220^\circ$ ; sublimable; easily soluble in alcohol, but not easily in water; is converted by boiling with water into alcohol and double oxalate of ammonia.

*Oxamate of Amyl* (Oxamylan) crystallizes in formless crusts.

*Ether-oxalic Acid*:  $\text{HO}(\text{AeO}, \text{OxO}_3)\text{OxO}_3$ . If to a solution of oxalate of ethyl in anhydrous alcohol, be added half enough potassa to saturate the oxalic acid, Ether-oxalic acid. thus separates ethyl-oxalate of potassa. If this be dissolved

in aqueous alcohol, then the potassa accurately precipitated by sulphuric acid, the solution will contain ether-oxalic acid, which, by evaporation, decomposes into alcohol and oxalic acid.

*Amyloxyd-oxalic Acid*:  $\text{HO}(\text{AmO}, \text{OxO}_3) \sim \text{OxO}_3$ . Isolated it is unknown. The potassa salt crystallizes in beautiful rectangular leaflets.

*Oxalate of Bichloroxide of Chloracetyl* (Chloroxal-  
Oxalate of bi- ether):  $\text{C}_4\text{Cl}_3 \left\{ \begin{smallmatrix} \text{Cl} \\ \text{O} \end{smallmatrix} \right\}^2, \text{OxO}_3$ , is obtained by the action  
chloroxide of chloracetyl.

of chlorine in the sunlight upon oxalate of ethyl. Colorless, tasteless, and inodorous substance; not acid; crystallizing in four-sided leaflets; melts at  $144^\circ$ ; insoluble in water. At a high temperature decomposes into carbonic oxide, oxychlor-carbonic acid, and bioxychloride of chloracetyl (chloraldehyd)  $\text{C}_4\text{Cl}_3 \left\{ \begin{smallmatrix} \text{Cl} \\ \text{O}_2 \end{smallmatrix} \right\}$ , and by boiling with solution of potassa, it separates into chloride of potassium, chloracetic acid, terchloride of formyl, and formic acid. Treated with anhydrous ammonia, it forms, besides other products, the so-called *chloroxalamid*.

*Chloracetyl-bichloroxyd-oxalic Acid* (Chloracetyl-  
Chloracetylbi- bichloroxydkleesäure, G., Chloroxal-tartaric Acid):  
chloroxyd-oxa-  
lic acid.  $\text{HO}, (\text{C}_4\text{Cl}_3 \left\{ \begin{smallmatrix} \text{Cl} \\ \text{O} \end{smallmatrix} \right\}^2, \text{OxO}_3) \sim \text{OxO}_3$ , is obtained simultane-

ously with chloracetic acid and hydrochloric acid by the action of alcohol upon the preceding compound. The anhydrous acid appears as a colorless, oily fluid; the hydrate crystallizes in small, colorless needles; soluble in all proportions in water, alcohol, and ether; tastes extremely burning; put upon the skin, it leaves a white spot.

*Chloroxalamid* (Chloroxethamid, Chloroxamethan):  
Chloroxalamid.  $(\text{C}_4\text{Cl}_3 \left\{ \begin{smallmatrix} \text{Cl} \\ \text{O} \end{smallmatrix} \right\}^2, \text{OxO}_3) + \text{NH}_2, \text{OxO}_2 = \text{C}_8\text{Cl}_5\text{NO}_6$ . By

spontaneous evaporation of the alcoholic solution, it is deposited as a white crystalline, snow-like body; of bitter-sweet taste; melts at  $143^\circ$ ; boils at  $200^\circ$ ; sublimable; easily soluble in alcohol, ether, and boiling water. Left a long time in contact with aqueous ammonia, it forms by decomposition of water, chloroxaltartrate of ammonia; a white crystalline substance.

Compounds of By the action of *chlorine* upon an aqueous solution  
oxalic acid, of citric acid, an oil-like, colorless, and strong smell-  
which are ing body is formed, which consists of  $\text{C}_8\text{Cl}_5\text{O}_3$ , and  
formed by the can be considered a compound  $= \text{C}_2\text{Cl}_2 \cdot (\text{C}_4\text{Cl}_3)\text{Cl}_3$ ,  
action of chlo-  $\text{OxO}_3$ ; it forms with 3 atoms HO leafy crystals,  
rine upon citric which at  $15^\circ$  melt under the loss of water. If a  
and itaconic solution of citrate of soda be treated with chlorine,  
acid. we thus obtain carbonic acid, chloride of sodium,  
acid citrate of soda, and an oily product of sweet etheric odor,

which, however, becomes insupportable in proportion as the decomposition advances; at the same time, we find in the solution an acid, which must consist of  $C_4H_2O_3 = C_2H_2 \cdot \text{OxO}_3$ . If the oily product be distilled, at first terchloride of formyl goes over, and later a colorless, mobile fluid, smelling like mustard-oil, of a sharp taste, and which consists of  $C_{10}Cl_8O_4 = 2(C_2Cl_2, C_2 \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right\}) + C_2O_2 (?)$ . Both compounds give, with an alcoholic potassa solution, chloride of potassium, and a new acid, which consists of  $C_4Cl_2O_3 = C_2Cl_2 \cdot C_2O_3$ . If bromine be left to act upon an aqueous solution of citrate of an alkali, we obtain, accompanied by evolution of carbonic acid and production of bromide of formyl, a crystallizable substance, which consists of  $C_6HBr_5O_4 = (C_2H)Br_3 + C_2 \left\{ \begin{smallmatrix} O \\ Br_2 \end{smallmatrix} \right\} + C_2O_3 (?)$ . By the action of *bromine* upon *itaconic* and *hydrate of citricic acid*, we obtain a heavy, yellow oil  $= C_6H_3Br_3O_2 = (C_4H_3)Br_3 + C_2O_2 (?)$ .

## PAIRED COMPOUNDS OF OXALIC ACID.

A series of acids can be considered as paired compounds of oxalic acid. These acids are mostly non-volatile, are distinguished by strongly acid properties; often they produce acid salts like oxalic acid; and, under the influence of alkalies, they easily decompose into oxalic acid. The constitution of the pairings is least known, therefore it is conformable with the present state of our knowledge to choose the simplest expression for their constitution, and be content at present with the empirical formulæ. In this group are found several interesting isomeric compounds. Among the most important acids of this group are:—

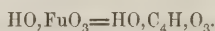
Fumaric Acid,	$C_4H_2O_3 = C_2H_2 \cdot \text{OxO}_3$ ,
Parafumaric “	$C_4H_2O_3 = C_2H_2 \cdot \text{OxO}_3$ ,
Aconitic “	$C_4H_2O_3 = C_2H_2 \cdot \text{OxO}_3$ ,
Malic “	$C_4H_2O_4 = C_2H_2O_2 \cdot \text{OxO}_3$ ,
Tartaric “	$C_4H_2O_5 = C_2H_2O_2 \cdot \text{OxO}_3$ ,
Racemic “	$C_4H_2O_5 = C_2H_2O_2 \cdot \text{OxO}_3$ ,
Itaconic “	$C_5H_2O_3 = C_2H_2 \cdot \text{OxO}_3$ ,
“	$= (C_6H_4 \cdot \text{OxO}_3) \cdot \text{OxO}_3$ ,
Citricic “	$C_5H_2O_3 = C_3H_2 \cdot \text{OxO}_3$ ,
Pyrotartaric “	$C_5H_3O_3 = C_3H_3 \cdot \text{OxO}_3$ ,
“	$= (C_6H_6 \cdot \text{OxO}_3) \cdot \text{OxO}_3$ ,
Komenic “	$C_6H_4O_4 = C_4H_2O_2 \cdot \text{OxO}_3$ ,
Pyroracemic “	$C_6H_3O_5 = C_4H_3O_2 \cdot \text{OxO}_3$ ,
Citric “	$C_6H_3O_6 = C_4H_3O_3 \cdot \text{OxO}_3$ ,
Saccharic “	$C_6H_4O_7 = C_4H_4O_4 \cdot \text{OxO}_3$ ,
Mucic “	$C_6H_4O_7 = C_4H_4O_4 \cdot \text{OxO}_3$ ,
Chelidonic “	$C_7H_4O_5 = C_5H_2O_2 \cdot \text{OxO}_3$ ,
	$= (C_{10}H_2O_4 \cdot \text{OxO}_8) \cdot \text{OxO}_3$ ,



Meconic Acid,	$C_7H_6O_6 = C_5HO_3, \sim O_xO_3,$
Pyromucic “	$C_{10}H_3O_5 = C_2H_2O_2, \sim (C_6, C_2H)O_3,$
Pyromeconic “	$C_{10}H_3O_5 = C_2H_2O_2 \sim (C_6, C_2H)O_3,$
Chinic “	$C_{14}H_{10}O_{10},$
Veratric “	$C_{18}H_9O_7,$
Opianic “	$C_{20}H_8O_9,$

Besides a few acids but little known.

#### FUMARIC ACID:



*Fumaric Acid* (Lichenic Acid) is found in *Fumaria officinalis*, in the herb *Glaucium luteum*, in Iceland moss (*Cetraria Islandica*), and is formed by dry distillation of malic acid. By pressing the fresh herb of the *Fumaria off.*, a juice is obtained which is boiled and strained, the lime precipitated by oxalate of potassa, and then from the filtrate the fumaric acid is precipitated by acetate of lead, and the procured lead salt decomposed by hydrosulphuric acid. Crystallizes from the hot aqueous solution in thin columns, tastes very sour, dissolves in 200 parts cold water, in 21 parts alcohol, is also soluble in ether and in nitric acid of 1.40 sp. gr. By heating above  $200^\circ$  it is converted into anhydrous parafumaric acid. A very permanent acid, which is not attacked by boiling nitric acid. *Lime water*, *baryta water*, and *strontian water*, as well as solutions of chloride of *barium* and of *calcium*, are not precipitated by fumaric acid; but, on the contrary, one part of the acid, dissolved in 200,000 parts water, gives a precipitate with *nitrate of silver*. All fumaric acid salts yield the bases to mineral acids accompanied by precipitation of fumaric acid.

*Fumarate of Ammonia*. If the neutral solution be evaporated, the acid salt crystallizes in six-sided columns; easily soluble in water and alcohol.

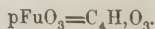
*Fumaramid*.  $NH_2, FuO_2$ , crystallizes in shining scales; insoluble in water and alcohol. It is obtained if fumarate of ethyl be left a little time in contact with aqueous ammonia.

*Fumarate of Potassa*:  $KO, FuO_3 + 2aq$ , crystallizes in small shining columns; easily soluble in water.

The *Acid Salt*:  $KO, HO, 2FuO_3$ , crystallizes; not easily soluble in water.

*Fumarate of Ethyl*:  $AeO, FuO_3$ . An oily fluid, heavier than water; of agreeable odor, like apples.

#### PARAFUMARIC ACID:



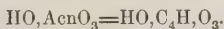
*Parafumaric Acid* is obtained in a water-free state, if fumaric acid be a long time heated above its melting point. Is also pro-

duced by sudden heating of malic acid to  $200^{\circ}$ . It collects in the receiver a colorless fluid, which stiffens to large crystals; melts at  $75^{\circ}$  and boils at  $176^{\circ}$ .

The *hydrate*,  $\text{HO}, p\text{FuO}_3$ , crystallizes in colorless, transparent, oblique, rhombic prisms; easily soluble in water, alcohol, and ether, and of very sour and disgusting taste. If it be heated a long time in a tall vessel, so that the water can continually flow back again, it is converted into hydrate of fumaric acid.

Probably *fumaric acid* consists of  $\text{C}_8\text{H}_2\text{O}_6 = (\text{C}_4\text{H}_2, \text{OxO}_3) \sim \text{OxO}_3$ ; it is then a double acid and saturates 2 atoms base; and the *salts* consist of  $\text{RO}, \text{HO}, \text{FuO}_6$  and  $2\text{RO} + \text{FuO}_6$ . It also gives several double salts.

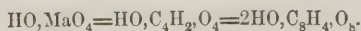
#### ACONITIC ACID:



*Aconitic Acid* (Citricinic Acid) is found in *Aconitum napellus* and *Stoerkeanum*, in *Equisetum fluviatile* and *limosum*, and is produced by decomposition of citric acid. The expressed juice of aconitum is evaporated to the consistency of thin extract; the aconite of lime crystallizes; a solution of this is precipitated by acetate of lead, and the lead salt decomposed by hydrosulphuric acid. Crystallizes from the etheric solution in irregular grains; colorless; inodorous; of pure acid taste; soluble in water, alcohol, and ether; non-volatile, and by heating decomposes into itaconic, citricic, and carbonic acid. With the *alkali bases* aconitic acid gives easily soluble salts, which, with nitrate of silver and acetate of lead, produce white precipitates, which, after a little time, become crystalline. Gives, with *potassa*, an acid salt, which consists of  $\text{KO}, 3\text{AcnO}_3$ .

*Aconate of Ethyl*:  $\text{AeO}, \text{AcnO}_3$ . If  $\frac{1}{2}$  part citric acid,  $\frac{3}{4}$  part alcohol, and  $\frac{1}{4}$  part sulphuric acid be a long time distilled, and the fluid which has gone over constantly poured back into the retort, we thus obtain aconate of ethyl, which is cleansed by washing with water and dried in a vacuum over sulphuric acid. Colorless fluid, smells like calamus, tastes very bitter; sp. gr. 1.074; boils at  $230^{\circ}$ , and volatilizes under partial decomposition.

#### MALIC ACID:



*Malic Acid* is an extensively diffused organic acid; it is found in nearly all sour juices, mostly, however, in company with tartaric, citric, and oxalic acid, etc.; the sour taste of the unripe apple, plum, and thornberry, the unripe sorb apple, the currant, whortleberry, etc., is principally produced by malic and citric acid; in most

plants it is met with in combination with lime. Artificially, it is not yet with certainty produced.

The juice of the not quite ripe sorb apple (*Sorbus aucuparia*) is best adapted to the production of malic acid. The juice is mixed with so much lime-water that the mass still shows a slight acid reaction, and the mixture kept boiling a few hours. We obtain the neutral malate of lime as a white sandy powder, which is immediately taken out with a spoon. It is washed with cold water and dissolved in warm dilute nitric acid (1 part acid to 10 parts water) to saturation. During the cooling, acid malate of lime separates in colorless crystals. The malate of lead obtained by decomposition of this salt by acetate of lead, is decomposed by hydrosulphuric acid, and the aqueous solution filtered from the sulphide of lead is evaporated upon the water-bath to the consistency of syrup; after a little time a solid crystalline mass of hydrate of malic acid is formed.

From the juice of the house-leek (*Sempervivum tectorum*) and from that of the apple malic acid can be procured in the same manner.

Malic acid is only with difficulty to be obtained in distinct crystals; it is colorless; easily soluble in alcohol and water; possesses a strong acid taste; at  $176^{\circ}$  it decomposes into water, fumaric and parafumaric acid. Nitric acid easily converts it into oxalic acid. Warmed with sulphuric acid, it decomposes into carbonic oxide and acetic acid; it reduces oxide of gold. Fused with hydrate of potash, it decomposes into acetic and oxalic acid. Upon the conversion of malic acid into succinic acid, *vide* Succinic Acid.

*Malic Acid Salts.* Malic acid forms neutral  $(RO, MaO_4)$  and acid  $(RO, HO, 2MaO_4)$  salts; it produces in acetate of lead a white precipitate, which, after long standing, becomes crystalline; melts in boiling water, mostly dissolves, and after cooling crystallizes in flat needles, or long scales. Almost all the salts are soluble in water.

*Malate of Ammonia.* The neutral compound,  $NH_4, O + MaO_4$ , appears as a deliquescent mass. The acid salt,  $NH_4, O, HO, 2MaO_4$ , forms beautiful water-clear crystals; soluble in 8 parts water, insoluble in alcohol.

The Neutral Potassa Salt,  $KO, MaO_4$ , is not crystallizable, deliquescent. The acid potassa salt,  $KO, HO, 2MaO_4$ , crystallizes, easily soluble in water, insoluble in alcohol. *Malate of baryta*,  $Ba, O, MaO_4 + aq$ . Crystalline scales, easily soluble in water. *Malate of lime.* If malic acid be saturated with chalk, an anhydrous salt is precipitated as a sandy powder almost insoluble in water. If the acid salt be saturated with carbonate of potash, after evaporation we obtain hard shining crystals, which consist of  $2(Ca, O, MaO_4) + 5aq$ . The acid lime salt,  $CaO, HO, 2MaO_4 + 6aq$ , is deposited from the nitric acid solution in large transparent crystals.

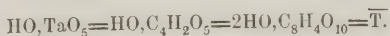
*Malate of Lead*:  $\text{PbO}, \text{MaO}_4 + 3\text{aq}$ . The voluminous precipitate which is formed by adding malate of potassa to a solution of acetate of lead changes after some time by gentle heat into colorless transparent prisms of silken lustre. If the salt be heated to  $220^\circ$  it is converted under loss of water into fumaric acid salt.

*Malamid* (Asparagin, Althaein):  $\text{NH}_2, \text{MaO}_3$ , is found in the young asparagus shoots, in licorice root, osteocolla root, and althea root, in the radicals of the vetch, etc. The expressed and filtered juice of asparagus is evaporated to syrup thickness and the residue left a long time in a cool place. We obtain crystals of asparagin, which are purified by recrystallization. Colorless, inodorous, rectangular, octohedral crystals containing 2 atoms water which they lose at  $100^\circ$ ; of insipid taste, very friable, grates between the teeth, soluble in 58 parts water, more easily soluble in alcohol, insoluble in pure ether. If *nitrous acid* be conducted into the solution, we obtain malic acid under evolution of nitrogen gas. If asparagin be warmed with the strong acids, we thus obtain ammonia salts and malaminic acid (asparagic acid); likewise act the strong alkalis. Asparagin possesses the capability of forming loose chemical combinations with acids and bases.

*Malaminic Acid* (Asparagic Acid):  $\text{HO}(\text{NH}_2, \text{MaO}_3) \text{---} \text{MaO}_4$ . We boil asparagin with baryta water until no more ammonia is evolved. From the hot filtered solution the baryta is precipitated by sulphuric acid; during the cooling, the asparagic acid is deposited in tasteless, inodorous crystals of mother-of-pearl lustre, and which dissolve in 128 parts cold water; non-volatile. Almost all the salts are soluble in water and possess a taste like meat broth. The *potassa salt* deliquesces. The *soda* and the *ammonia salt* are crystallizable. The lime salt is a gum-like mass.

Probably *cynodin*, which is found in the root of *Cynodon dactylon*, is identical with asparagin.

## TARTARIC ACID:



*Tartaric* is, like malic acid, widely diffused in nature. It is found in addition to malic and citric acid in almost all sour fruits, partly free as in the juice of the tamarind, in pepper, in pineapple, in the juice of unripe grapes, partly combined with potassa as in grape juice, in sorrel, in the mulberry, in the root of *Triticum repens*, *Leontodon taraxacum*, in the berries of *Rhus coriaria*, etc. Artificial production of tartaric acid is not yet proved with certainty. We obtain tartaric acid from tartrate of potassa (acid tartrate of potash) in the same way as the oxalic acid from the oxalic salts (*v.* Oxalic Acid). Tartaric acid crystallizes from the syrup-thick solution in remarkably beautiful, large, rhombohedral, thermoe-



lectrical crystals, which dissolve in  $\frac{7}{13}$  part cold water, and easily in alcohol; of strong acid taste; it possesses in a remarkable degree the capability of turning to the right the polarization's plane of light, which property increases by warming the substance and by combination with bases. Upon the changes which tartaric acid suffers by gentle melting, v. below tartral and tartrelic acid. Heated to  $200^{\circ}$  or  $300^{\circ}$  it decomposes into water, carbonic acid, pyroracemic acid,  $C_6H_3O_5$ , and pyrotartaric acid,  $C_5H_3O_3$ ;  $C_8H_4O_{10} = C_6H_3O_5 + HO + 2CO_2$ . If the temperature be very high, we obtain acetic acid, hydrocarbon, empyreumatic oils, etc. If tartaric acid be intimately mixed with platinum black, by heating there are evolved water, carbonic acid, pyrotartaric acid and pyroracemic acid. Neutral tartrate of potassa mixed with some yeast begins to ferment at  $15^{\circ}$ ; under evolution of hydrogen gas we obtain butyric acid. *Nitric acid* immediately decomposes tartaric acid into oxalic and carbonic acid. A mixture of 1 atom tartaric acid with 2 atoms *superoxide of lead* at  $12$  or  $15^{\circ}$  comes in a few moments to glowing, and ceases to glow under evolution of carbonic and formic acid (v. Formic Acid). *Chlorine* does not decompose tartaric acid. *Bromine* brought together with simple tartrate of potassa, forms bromide of potassium and acid tartrate of potassa. If tartaric acid be warmed with a little hydrate of *sulphuric acid*, there is evolved under blackening of the acid a mixture of carbonic oxide, carbonic acid, and sulphurous acid. If tartaric acid be cautiously warmed with much sulphuric acid, no blackening takes place, and there is evolved a mixture of 4 parts carbonic oxide to 1 part sulphurous acid. Fused with *hydrate of potassa*, it decomposes into acetic acid, oxalic acid, and water.

Tartaric acid  
salts with or-  
ganic bases.

*Tartrates.* Tartaric acid is among the strongest organic acids; it has a great tendency to form acid salts and double salts; with potassa and ammonia, it forms neutral salts easily soluble, and acid salts not easily soluble. Hence if tartaric acid be added in excess to a solution of potassa, a white crystalline precipitate of tartrate of potassa is formed which is soluble in alkalies as well as in acids. The combinations with the alkaline earths and oxides of heavy metals, are in the simple state insoluble in water, or soluble with difficulty; but they dissolve in free tartaric acid, in mineral acids, and in alkalies. The tartaric acid double salts are obtained by saturation of the acid salts with a base. Tartaric acid prevents the precipitation of oxide of iron and other metallic oxides by ammonia.

*Simple Tartrate of Ammonia:*  $NH_4O, TaO_5$ , crystallizes; more easily soluble in cold than in hot water.

*The Acid Salt:*  $NH_4O, HO, 2TaO_5$ , requires 200 parts water for solution.

*Simple Tartrate of Potassa* (Tartarus tartarisatus):  $KO, TaO_5$ .

From the concentrated solution forms large crystals, which belong to the rhombic system; at  $15^{\circ}$  100 parts water dissolve 133 parts of the salt.

*Bitartrate of Potassa* (Crystalli-tartari, Cream of Tartar):  $\text{KO}, \text{HO}, 2\text{TaO}_5$ , is procured by purification of *crude tartar*; appears in white, rhombic crystals; dissolves in 204 parts water at  $19^{\circ}$ , in 89 parts at  $25^{\circ}$ , in 37 parts at  $50^{\circ}$ , and in 15 parts at  $100^{\circ}$ ; easily soluble in dilute mineral acids.

*Tartrate of Potassa-boracic-acid* (Tartarus Boraxatus):  $\text{KO}, \text{TaO}_5 + \text{BoO}_3, \text{TaO}_5$ , remains behind as a pasty mass, if equal atoms of tartrate of potassa and crystallized boracic acid be dissolved in water, and the solution completely evaporated to dryness upon the water-bath.

*Tartrate of Potassa-ammonia* (Tartarus Ammoniatus):  $\text{KO}, \text{NH}_4\text{O}, 2\text{TaO}_5$ , crystallizes in water-clear four or six-sided prisms; easily soluble in water; loses ammonia in a current of dry air, leaving supertartrate of potassa behind.

*Tartrate of Soda*:  $\text{NaO}, \text{TaO}_5 + 2\text{aq}$ , crystallizes in water-clear columns; dissolves in 5 parts cold water, and in every proportion in boiling.

*Bitartrate of Soda*:  $\text{NaO}, \text{HO}, 2\text{TaO}_5$ , crystallizes in six-sided prisms; dissolves in 8 parts cold water and in 1.8 parts boiling.

*Tartrate of Soda-potassa* (Sal Seignette):  $\text{KO}, \text{NaO}, 2\text{TaO}_5 + 8\text{aq}$ , crystallizes in large water-clear prisms with many side planes, and with end-planes set direct; soluble in  $2\frac{1}{2}$  parts cold and less boiling water; the salt loses at  $100^{\circ}$  6 atoms water.

*Tartrate of Lime*:  $\text{CaO}, \text{TaO}_5$ , is obtained by double decomposition; scarcely soluble in water. If the hydrochloric acid solution be saturated with ammonia, after a little time the tartrate of lime separates in small crystals, which contain 4 atoms water.

*Tartrate of Alumina*:  $\text{Al}_2\text{O}_3, 3\text{TaO}_5$ , a gum-like mass, not deliquescent; easily soluble in water; serves as a mordant, and is generally obtained by mixing 2 parts tartaric acid with 8 parts alum.

*Tartrate of Protoxide-of-Iron-potassa* (Tartarus Martialis):  $\text{KO}, \text{FeO}, 2\text{TaO}_5$ . A white powder, not easily soluble in water. It is obtained by boiling iron-filings, tartar, and water, and evaporating the solution.

*Basic-tartrate of Antimony*:  $\text{SbO}_3, \text{TaO}_5 + \text{aq}$ . A solution of oxide of antimony in tartaric acid is mixed with alcohol; the basic salt separates as a white granular powder, which at  $100^{\circ}$  loses 1 atom water. If the salt be exposed to a temperature of  $190^{\circ}$ , another atom water escapes, and the compound, which remains then, consists of  $\text{SbO}_3, \text{C}_4\text{HO}_4$ . If we regard tartaric acid as a paired oxalic acid  $= (\text{C}_2\text{H}_2, \text{O}_2)^- \text{C}_2\text{O}_3$ , the new acid consists of  $(\text{C}_2\text{H}, \text{O}) \text{C}_2\text{O}_3 = (\text{C}_2\text{H}, \text{O}_2)^- \text{C}_2\text{O}_2$ ; by absorption of water, it is again converted into tartaric acid. Basic-tartrate of antimony gives

with tartrates double salts, which all lose at  $200^{\circ}$  2 atoms water from the constituents of 2 atoms tartaric acid.

*Basic-tartrate of Antimony-potassa* (Tartar Emetic):  $\text{KO}, \text{SbO}_3, 2\text{TaO}_5 + \text{aq}$ , is obtained when equal parts tartar and oxide of antimony are a long time digested with water, and the mass dissolved in boiling water. Forms large crystals; soluble in 14 parts cold water and 1.88 parts boiling; loses at  $100^{\circ}$  1 atom and at  $222^{\circ}$  3 atoms water. Alkalies completely precipitate the oxide of antimony from tartar emetic; and if the latter be brought together with an acid, thus would all the oxide of antimony be precipitated as basic salt, whilst acid tartrate of potash is formed.

*Tartrate of Potassa-arsenious-acid*:  $\text{KO}, \text{AsO}_3, 2\text{TaO}_5$ , is obtained by boiling arsenious acid and supertartrate of potassa.

*Methyloxyd-tartaric Acid*:  $\text{HO}(\text{MeO}, \text{TaO}_5)^- \text{TaO}_5$ .  
 Combinations of tartaric acid with oxides of the methyl group. is obtained, when equal weight of tartaric acid and wood-spirit are boiled, until the tartaric acid is dissolved, and then the solution evaporated upon the water-bath to syrup-thickness. The whole mass changes into colorless prismatic crystals; easily soluble in water, alcohol, and wood-spirit. The *potassa salt* crystallizes in colorless prisms; even so the *baryta salt*. Both are decomposed by boiling with water.

*Tartrate of Ethyl*:  $\text{AeO}, \text{TaO}_5$ , forms a brown, inodorous mass, not sour, and of a bitter taste. It is obtained if 7 parts alcohol, 6 parts tartaric acid, and 2 parts sulphuric acid are a long time boiled, the mass diluted with water, accurately saturated with potassa, evaporated, and the tartrate of ethyl extracted from the residue by alcohol.

*Ether-tartaric Acid*:  $\text{HO}(\text{AeO}, \text{TaO}_5)^- \text{TaO}_5$ , is obtained like methyloxyd-tartaric acid; the tartaric acid yet present precipitated by baryta. Crystallizes in beautiful, long prisms; inodorous, of sweetish acid taste; easily soluble in water, rather permanent; by long boiling with water decomposes into alcohol and tartaric acid.

The *potassa salt* crystallizes in rhomboidal prisms; the *baryta salt* in rhomboidal tables of mother-of-pearl lustre.

*Amyloxyd-tartartaric Acid*:  $\text{HO}(\text{AmO}, \text{TaO}_5)^- \text{TaO}_5$ , appears as a syrup-like fluid of intolerable bitter taste.

*Metatartaric Acid*:  $\text{HO}, \text{C}_4\text{H}_2\text{O}_5$ . Tartaric acid dried at  $100^{\circ}$ , is heated in an oil-bath to melting (at  $170$  to  $180^{\circ}$ ), and then we withdraw it immediately from the heat; thus we obtain a transparent glass-like mass, which deliquesces, and is again converted into ordinary tartaric acid. The salts of metatartaric acid are more soluble in water than those of the ordinary acid, and have another form.

*Tartralic Acid*:  $\text{C}_8\text{H}_6\text{O}_{12} = \text{HO}(\text{C}_4\text{H}_3\text{O}_6)^- \text{C}_4\text{H}_2\text{O}_5 = \text{HO}, \text{C}_8\text{H}_5\text{O}_{11}$ . If a few grammes tartaric acid be heated in a porcelain bowl under stirring to  $200^{\circ}$ , we obtain a mass not crystallizable, which

deliquesces, and with bases produces salts consisting of  $\text{RO}, \text{C}_8\text{H}_5\text{O}_{11}$ . The salts, in aqueous solution, change into acid tartrates. Forms soluble salts with lime and baryta.

*Tartrelic Acid*:  $\text{C}_8\text{H}_4\text{O}_{10} = \text{HO}, \text{C}_8\text{H}_3\text{O}_9$ , is obtained when tartaric acid is a little time maintained in a fused condition at  $180^\circ$ . Strongly acid; crystallizable; changes, by absorbing water, first into tartralic and then into common tartaric acid. This acid saturates 1 atom base. If the aqueous solution of the acid be treated with acetate of lime or baryta, insoluble tartrelic acid salts are formed, which fall in the form of a syrup.

*Anhydrous Tartaric Acid*:  $\text{C}_4\text{H}_2\text{O}_5 = \text{HO}, \text{C}_4\text{HO}_4(?)$ . Fifteen or twenty grammes pulverized tartaric acid, in a porcelain bowl, is quickly heated over glowing coal until it is converted into a swollen white mass, which process must be terminated in four or five minutes. The mass is treated with water, which dissolves the tartralic acid yet present, whilst the anhydrous tartaric acid remains behind. It is not soluble in water, alcohol, and ether; does not combine with bases; it tastes slightly sour, and reddens litmus. In contact with water, it is by degrees converted into tartrelic, tartralic, and ordinary tartaric acid.

#### ANTITARTARIC ACID:



We saturate acid racemate of potassa with soda or ammonia; thus, after evaporation, is formed in the cold equal quantities of two salts. One is the ordinary tartaric, the other the antitartaric acid double salt. Both have the same crystal form, but with certain hemiëdral planes which lie to the right in tartaric acid double salts, and to the left in those of antitartaric acid; the first in aqueous solution turns polarized light to the right, the latter to the left; but if we unite both salts, we obtain racemic acid salts, and the rotation = 0. If pure antitartaric acid be procured, it has all the properties of tartaric acid, but it turns polarized light as strongly to the left as tartaric acid does to the right, an appearance which occurs in all antitartaric acid salts, which otherwise agree with those of tartaric acid.

#### RACEMIC ACID



*Racemic Acid* (Paratartaric Acid) can, as follows from what is here communicated, be viewed as a compound of tartaric acid and antitartaric acid, and must then be regarded as a double salt similar to succinic acid. The acid was in the years 1822 to 1824



obtained in the tartaric acid factory of Thann, in Vogesen, from tartar, which, instead of acid tartrate of potassa, was acid racemate of potassa. Later the acid was no more procured; however, the ordinary tartar appears to contain often small quantities of acid racemate of potassa. Racemic acid crystallizes from the aqueous solution in water-clear, oblique, rhombic columns containing 1 atom water of crystallization, which is lost at  $100^{\circ}$ , leaving the hydrate as an effloresced inodorous mass. It possesses a strong sour taste, and, in most respects, agrees with tartaric acid.

Difference between racemic and tartaric acid.

But it differs in the following particulars: 1. Tartaric acid in aqueous solution turns polarized light to the right; racemic acid possesses no power of rotation. 2. Tartaric acid requires  $\frac{7}{13}$ , racemic acid  $5\frac{1}{4}$  parts cold water for solution. 3. The crystals of racemic acid effloresce in warm air; those of tartaric acid suffer no change. 4. The two acids differ in crystal form. 5. In a solution of racemate of lime in dilute hydrochloric acid, ammonia immediately produces a white crystalline precipitate; tartrate of lime is not precipitated till after some time. 6. Racemic acid precipitates a solution of gypsum; tartaric acid does not. 7. Lime-water added in excess to racemic acid, gives a precipitate which does not dissolve in chloride of ammonium; but the precipitate from tartaric acid is soluble in that substance.

#### ITACONIC AND CITRACONIC ACID.

*Itaconic and citraconic acid* stand to each other in a similar proportion to fumaric and parafumaric acid, or to tartaric and racemic acid; they are isomeric, and both correspond to the formula:  $\text{HO}, \text{C}_5\text{H}_2, \text{O}_3 = 2\text{HO}, \text{C}_{10}\text{H}_4, \text{O}_6 = 2\text{HO}(\text{C}_6\text{H}_4, \text{OxO}_3) \sim \text{OxO}_3$ . The two acids differ principally in their different solubility in water. According to other researches, the two acids are said not to be different. Both acids, by dry distillation, form citric acid. It is probable that by the first action of heat they form aconitic acid, and this then, by farther heating, decomposes into itaconic and citraconic acid under production of carbonic acid; itaconic acid must first arise and this is transformed into citraconic acid.

Itaconic acid.

*Itaconic Acid* (Citric Acid):  $\text{HO}, \text{ItO}_3$ . Citric acid is heated in a retort until it shows yellow vapor. In the distillation it is necessary to take care that the itaconic acid passes immediately over and does not flow back again, because it otherwise is changed into citraconic acid. We obtain an oily distillate of anhydrous itaconic acid (?) and citraconic acid, whose separation by distillation is impossible. The distillate, which after a little time stiffens, is dissolved in sixfold weight of water, and the solution evaporated. At first we obtain crystals of hydrate of

itaconic acid, and by farther evaporation citraconic acid. The hydrate of itaconic acid crystallizes in octohedrons with rhombic bases; inodorous; tastes sharply acid; easily soluble in hot water, dissolves in 17 parts water of  $10^{\circ}$ , and in 12 parts of  $20^{\circ}$ ; easily soluble in alcohol, insoluble in ether; fuses at  $160^{\circ}$  to a colorless fluid, and volatilizes in white suffocating vapor. Upon the action of bromine upon a solution of neutral itaconate of potassa, compare page 284.

*Itaconic acid* gives with bases neutral and acid combinations, which have been but little investigated. *Salts of peroxide of iron* color itaconic acid red. Most of the salts are soluble in water. The *neutral potassa salt* forms a deliquescent salt, which does not crystallize. The *acid salt* appears in small shining leaflets. The *baryta salt*,  $\text{BaO}, \text{ItO}_3 + \text{aq}$ , crystallizes in long slender threads in stelliform groups.

*Itaconate of Ethyl*:  $\text{AeO}, \text{ItO}_3$ , exhibits a colorless fluid of agreeable aromatic odor and bitter taste; sp. gr. 1.050; boils at  $227^{\circ}$ .

*Citraconic Acid* (Citricic Acid). *Anhydrous*: Citraconic acid,  $\text{CtrO}_3$ . If the hydrate of itaconic acid be submitted to distillation, it decomposes into water and anhydrous citraconic acid; the former of which first escapes, and the latter passes over at  $200^{\circ}$ . Citraconic acid is also formed by dry distillation of lactic acid. Colorless, mobile, inodorous fluid; of caustic, sour, and astringent taste; sp. gr. 1.247; boils at  $212^{\circ}$ , but evaporates even at  $90^{\circ}$ .

The *hydrate*,  $\text{HO}, \text{CtrO}_3$ , whose production is given at itaconic acid, crystallizes in four-sided columns; decomposes at  $80^{\circ}$  into water and anhydrous acid. Soluble in all proportions in water, and easily soluble in alcohol and ether. Bromine behaves towards citraconic acid salts as to those of itaconic acid. Forms, with bases, neutral and acid salts.

If *ammonia gas* be conducted over *anhydrous citraconic acid*, we thus obtain a transparent glass-like body, which consists of  $\text{NH}_3 + 2\text{CtrO}_3$ .

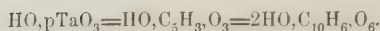
The *neutral potassa salt* is easily soluble in water; not crystallizable; the *acid salt* behaves in like manner.

The *baryta salt*,  $\text{BaO}, \text{CtrO}_3$ , is obtained if a boiling hot solution of citraconic acid be saturated with carbonate of baryta; after the cooling, it separates as a white crystalline powder.

The *acid baryta salt*,  $\text{BaO}, \text{HO}, 2\text{CtrO}_3 + \text{aq}$ , crystallizes from the hot solution in large, solid, wart-shaped groups.

*Citraconate of ethyl* quite agrees with itaconate.

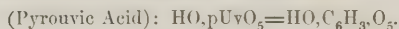
## PYROTARTARIC ACID:



*Pyrotartaric acid* is formed by dry distillation of tartaric acid and racemic acid, and is also said to be produced by long action of dilute nitric acid upon sebacic acid. It is metameric with lipinic acid. We submit tartaric acid to distillation at 200 to 300°. The distillate is repeatedly distilled until the residue becomes syrup-thick; then we change the receiver, and distil to dryness, and evaporate the last obtained distillate in a vacuum; we obtain crystals of pyrotartaric acid, which become pure by recrystallization. Small, colorless, inodorous needles, of sour taste, and in stelliform groups, and which melt at 100° and boil at 180°. Easily soluble in water and alcohol.

The statements respecting the properties of the pyrotartaric acid salts do not agree. A concentrated solution of the acid gives no precipitate with baryta-water, strontia-water, and lime-water, as well as with acetate of lead; vinegar of lead produces a cheese-like precipitate; it is said to form principally acid salts.

## PYRORACEMIC ACID

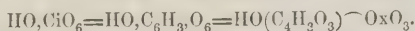


*Pyroracemic acid* is formed, if tartaric acid or racemic acid be distilled at 200 to 220°. The distillate, a mixture of pyrotartaric, pyrорacemic, and acetic acid, etc., is distilled upon the water-bath; it passes over pyrорacemic and acetic acid. If the mixture be digested with freshly precipitated, carbonate of lead, pyrорacemate of lead is precipitated, from which the acid is separated by hydrosulphuric acid. Appears as a thick, pale-yellow syrup; in the cold inodorous; smells by warming suffocatingly sour, like hydrochloric acid; tastes sharp, sour, and bitter; soluble in all proportions in water, alcohol, and ether. Suffers by distillation a partial decomposition under production of a brown syrup; likewise by evaporation of the aqueous solution.

Pyrорacemic acid expels acetic acid from its compounds. Most of the salts can be obtained in two modifications, one crystalline, and the other gummy; the latter cannot be again changed into the former. The crystalline is obtained, if in the production each warming be avoided; if the crystalline salt be boiled in the aqueous solution, it is converted into the gummy compound. The dry salts of both modifications, do not bear a high temperature, without becoming yellow; they all are colored at 120°. Sulphuric acid decomposes the dry acid only with difficulty. Most pyrорacemates of metallic oxides dissolve in pure alkalies and their

carbonates. The acid salts are mostly soluble in alcohol and ether; they redden litmus. The neutral insoluble salts are often decomposed even by water. If in the solution of the salt a small crystal of sulphate of protoxide of iron be placed, thus it is colored fire-red; sulphate of copper produces after some time a white precipitate.

## CITRIC ACID:



Citric acid is found in the juice of many sour-tasting fruits, as in that of lemons, oranges, in the fruit of *Prunus padus*, *Vaccinium vitis idæa*, in the tamarind in common with tartaric acid, in currants, in whortleberries, strawberries, mostly in company with malic acid. It is generally procured from lemon-juice. It is boiled with albumen, then filtered, and at  $90^\circ$  saturated with carbonate of lime. The citrate of lime which separates particularly by boiling, is, after washing, decomposed by sulphuric acid. From the hot, concentrated solution, the citric acid separates in large, water-clear crystals, whose primary form is the direct rhombic prism, and it corresponds to the formula  $\text{HO}, \text{C}_6\text{H}_3\text{O}_6$ . If the acid be left to crystallize by spontaneous evaporation of the aqueous solution, the crystals contain another atom of water of crystallization, which escapes at  $100^\circ$ . Citric acid possesses a strong, sour, agreeable taste, dissolves in 0.75 parts cold, and in 0.5 parts boiling water; soluble in alcohol, insoluble in ether. Power of rotation = 0. In the aqueous solution, citric acid decomposes, after a time, into acetic acid under formation of mould. It melts at  $150^\circ$ , and decomposes by the first action of heat into aconitic and carbonic acid, carbonic oxide, and acetone; by stronger heat the aconitic acid decomposes into itaconic and carbonic acid, and, on the other hand, into acetone, and carbonic oxide. With pumice-stone or platinum black, intimately mixed, the decomposition commences at  $150$  or  $160^\circ$  under evolution of carbonic acid. If it be treated a long time with concentrated nitric acid, it decomposes into oxalic, acetic, and carbonic acid and water. By dry distillation with peroxide of manganese and dilute sulphuric acid, ammonia is obtained under evolution of carbonic acid. It reduces oxide of gold. Upon the action of chlorine and bromine on citric acid, and citric acid salts, compare page 284. Heated with hydrate of potassa, it decomposes into oxalic and acetic acid.

*Citrates.* Citric acid combines with bases in three proportions, forming sesqui-uni- and bi-acid salts. If the sesqui-acid salts be exposed to a high temperature, 1 atom water leaves the acid, and its place is taken by 1 atom base, whereby they, at the same time, are



converted into uni-acid salts from  $3\text{RO} + 2\text{C}_6\text{H}_3\text{O}_6$  arises  $\text{RO}, \text{C}_6\text{H}_3\text{O}_6 + \text{RO}, \left\{ \begin{array}{l} \text{C H O} \\ \text{RO} \end{array} \right.$ . If the salt comes in contact with water, it thus changes again into ordinary sesqui-acid salts. *Sesquicitrate of potassa*,  $3\text{KO}, 2\text{CiO}_6$ , is obtained by spontaneous evaporation of a solution of citric acid saturated with carbonate of potassa. Forms stelliform groups of transparent, pointed crystals; tastes alkaline, deliquesces; insoluble in alcohol. The prot-acid potassa salt,  $\text{KO}, \text{CiO}_6$ , is obtained if a solution of the preceding salt be mixed with half as much more citric acid as it contains. Dried to an amorphous mass, it tastes agreeably sourish. The *bi-acid salt*,  $\text{KO}, \text{HO}, 2\text{CiO}_6 + 2\text{aq}$ , appears in large, prismatic crystals, completely transparent, tastes agreeably acid; slightly soluble in boiling alcohol; is obtained if to the prot-acid salt another atom of citric acid be added. *Citrate of soda* (containing 4 atoms base and 3 atoms of acid),  $4\text{NaO}, \text{HO} + 3\text{CiO}_6$ , forms a gummy mass of an agreeable sour taste. *Sesqui-citrate of potassa soda*,  $3\text{KO}, 2\text{CiO}_6 + 3\text{NaO}, 2\text{CiO}_6 + 4\text{aq}$ , crystallizes in stelliform prisms of silken lustre. *Sesquicitrate of lime*,  $3\text{CaO}, 2\text{CiO}_6 + 3\text{aq}$ , is obtained if a solution of simple citrate of potassa or soda be mixed with chloride of calcium; a crystalline powder more easily soluble in cold water than in boiling. If lime-water be accurately saturated with citric acid, no precipitate forms in the cold, but by heating, citrate of lime is deposited; likewise ammonia precipitates citrate of lime from its solution only in the heat. The *neutral citrate of lime*,  $\text{CaO}, \text{CiO}_6 + \text{aq}$ , forms leafy, shining crystals, and is obtained by dissolving the former compound in a warm solution of citric acid. Decomposes by washing with water into a white powder which consists of 5 atoms of lime and 4 atoms citric acid  $= 3\text{CaO}, 2\text{CiO}_3 + 2(\text{CaO}, \text{CiO}_6)$ .

Combinations  
of citric acid  
with oxides of  
the Methyl  
group.

*Citrate of Methyl*:  $3\text{MeO}, 2\text{CiO}_6$ , is obtained by the introduction of hydrochloric acid gas into a solution of citric acid in wood-spirit. Forms prismatic crystals. *Citrate of ethyl*:  $3\text{AeO}, 2\text{CiO}_6$ , is obtained in a similar manner. Colorless, oily liquid, of bitter, disagreeable taste, inodorous; sp. gr. 1.142. Decomposes at  $283^\circ$ . Easily soluble in alcohol.

### SACCHARIC ACID AND MUCIC ACID.

*Saccharic acid* and *mucic acid* are isomeric, and both correspond to the formula  $\text{HO}, \text{C}_6\text{H}_4\text{O}_7$ . The former is produced by the action of nitric acid upon sugar and the latter by the like action upon gum, mucilage of plants, and milk sugar.

*Saccharic acid.* *Saccharic Acid*:  $\text{HO}, \text{SaO}_7 = \text{HO}, \text{C}_6\text{H}_4\text{O}_7 = \text{HO} (\text{C}_4\text{H}_4\text{O}_4) \cdot \text{OxO}_3$ . We dissolve one pound sugar, by gentle heat, in a large bowl, in three pounds nitric acid of 1.25

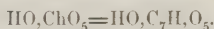
sp. gr.; as bubbles of nitric acid appear, the bowl is removed from the fire. When the first action is over and the temperature has fallen to  $50^{\circ}$ , we preserve this temperature so long as nitrous acid is evolved. Afterward the mass is mixed with water saturated with carbonate of potassa, and to the saturated solution some acetic acid added. After a few days, acid saccharate of potassa is deposited, which is purified by recrystallization. This salt is dissolved in water, the solution neutralized by potassa, precipitated by sulphate of cadmium, and the saccharate of cadmium decomposed by hydrosulphuric acid. Dries by evaporation in a vacuum over sulphuric acid to a brittle mass which, in the air, immediately becomes moist and viscid; tastes very sour, soluble in all proportions in water and alcohol. Is converted by boiling with nitric acid into oxalic acid, and decomposes by heating with concentrated potassa solution into oxalic and acetic acid. With bases it gives neutral and acid salts. The *neutral potassa salt*,  $\text{KO}, \text{SaO}_7$ , forms a white crystalline mass easily soluble in water. The *acid salt*,  $\text{KO}, \text{HO}, 2\text{SaO}_7$ , easily crystallizes, dissolves in 80 or 90 parts water. *Saccharate of baryta*,  $\text{BaO}, \text{SaO}_7$ , appears as a granular crystalline powder, soluble with difficulty, if a boiling solution of the neutral potassa salt be mixed with chloride of barium.

*Mucic Acid*:  $\text{HOMuO}_7 = \text{HO}, \text{C}_6\text{H}_4, \text{O}_7$ . Appears Mucic acid.  
as a sandy white powder, which reddens litmus and possesses a feeble acid taste; dissolves in 60 to 80 parts boiling water; by cooling  $\frac{1}{4}$  is deposited as a crystalline powder. Is obtained if gum or milk sugar be heated with 6 parts dilute nitric acid until the nitric acid has gone over. If we evaporate a hot saturated aqueous solution of mucic acid to dryness, and dissolve the residue in alcohol, there remains, after the spontaneous evaporation, a crystalline crust of *metamucic acid*; it has the same constitution as mucic acid, but tastes more acid, is more soluble in water, and also soluble in alcohol. If it be dissolved in boiling water, mucic acid is again separated by cooling. By dry distillation, mucic acid is decomposed into pyromucic acid,  $\text{C}_{10}\text{H}_3\text{O}_5$ , and an empyreumatic product. Mucic acid is weak, and *gives with bases* acid and neutral salts, mostly insoluble; the combinations with the alkalies are soluble. If to a solution of nitrate of protoxide of mercury a solution of mucic acid be added, immediately a copious white precipitate is formed; if the same experiment be made with the metamucic acid, after some time, a granular precipitate is formed. In general, the solubility of the metamucic acid salts is greater than that of the mucic acid salts. The *potassa salt* forms small neutral crystals soluble in hot water. The *soda salt* separates from the hot solution in crystalline crusts.

*Mucate of Methyl*:  $\text{MeO}, \text{MuO}_7$ . Crystallizes in flat, six-sided, rhombic prisms, easily soluble in boiling water and in 210 parts boiling alcohol; non-volatile.

*Mucate of Ethyl*:  $\text{AeO}, \text{MuO}_7$ . We gently heat mucic acid with fourfold its weight of sulphuric acid, and, after 12 hours, add 4 parts alcohol. After 24 hours the stiffened mass is shaken with water, whereby mucic ether is precipitated. Crystallizes from the alcoholic solution in water-clear, colorless, quadrilateral prisms, which taste bitter; melts at  $158^\circ$ ; easily soluble in alcohol and hot water, insoluble in ether; decomposes at  $170^\circ$  into water, alcohol, carbonic, pyromucic, and acetic acid, etc. *Chlorine* decomposes the compound.

#### CHELIDONIC ACID:



*Chelidonic acid* is found in *Chelidonium majus*, and in greatest quantity in the time of flowering. The expressed juice is boiled away, filtered, the filtrate acidulated with nitric acid, and then nitrate of lead added in small quantity, so long as a crystalline precipitate of chelidonate of lead with chelidonate of lime is formed. This is diffused in water, and decomposed by hydrosulphuric acid. The obtained solution of acid chelidonate of lime is neutralized with chalk, and, by evaporation and recrystallization, the pure chelidonate of lime procured; the same is decomposed by carbonate of ammonia, and the obtained ammonia salt mixed with hydrochloric acid, whereby the chelidonic acid is precipitated. It is purified by recrystallization from hot alcohol. Appears in long silky crystals, which contain 1 atom water of crystallization; inodorous, and of a strong acid taste; dissolves in 106 parts cold water, in 26 parts of boiling and in 709 parts alcohol. The acid decomposes at  $220$  to  $225^\circ$ ; it becomes soft under evolution of carbonic acid. It is not acted upon by *fuming nitric acid*, but briskly decomposed by dilute; also, is it dissolved by *concentrated sulphuric acid* without change.

*Chelodinic acid* is strong, and dissolves iron and zinc under evolution of hydrogen; it forms a few basic, neutral, and acid salts, and also gives like oxalic acid quadri-acid salts. The basic salts consist of 3 atoms base and 2 atoms acid, and are yellow; but they very easily yield 1 atom of base to the carbonic acid of the air, whilst neutral salts are formed. Many salts contain water of crystallization very intimately combined, and do not lose it at  $100^\circ$ . The *neutral ammonia salt* crystallizes in white prisms of a silky lustre; at  $160^\circ$  carbonic acid is evolved under formation of a new acid.

*Sesqui-chelidonate of Potassa*:  $3\text{KO}, 2\text{ChO}_5$ . It separates, if to a solution of the neutral salts an alcoholic potassa solution be added; forms amber-yellow crusts.

*Proto-chelidonate of Soda*:  $\text{NaO}, \text{ChO}_5 + 4\text{aq}$ , is obtained by

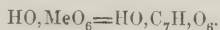
decomposition of the neutral potassa salt by carbonate of soda; fine needles of silky lustre; easily soluble in water.

The *Bichelidonate of Soda*:  $\text{NaO}, \text{HO}, 2\text{ChO}_5 + 4\text{aq}$ , crystallizes in fine needles, which are deposited, if to the neutral salt  $\frac{1}{3}$  d part chelidonic acid be added; by recrystallization it decomposes into *proto-* and *quadri-acid salts*,  $\text{NaO}, 3\text{HO}, 4\text{ChO}_5 + 5\text{aq}$ , which crystallize in fine needles.

*Simple Chelidonate of Lime*:  $\text{CaO}, \text{ChO}_5 + 3\text{aq}$ . Its production is above given. Forms in prismatic crystals of silky lustre; soluble with difficulty in cold water, and easily soluble in boiling.

The *quadri-acid salt*:  $\text{CaO}, 3\text{HO}, 4\text{ChO}_5 + 3\text{aq}$ , crystallizes in needles.

#### MECONIC ACID:



*Meconic acid* contains 1 atom more of oxygen than chelidonic acid. It is found in opium. To a concentrated cold aqueous extract of opium we add chloride of calcium, whereby a mixture of meconate and sulphate of lime is precipitated. The precipitate, washed with water and alcohol, is treated with water of  $90^\circ$ , and some hydrochloric acid; we obtain a solution of acid meconate of lime, which, during cooling, is deposited in crystals; if these are several times treated with water of  $90^\circ$ , and some hydrochloric acid, we obtain pure meconic acid. It crystallizes from the aqueous solution in beautiful white, transparent micaceous scales, which contain 2 atoms water. Inodorous; tastes slightly sour; dissolves in 4 parts hot water, and imparts a deep-red color to salts of peroxide of iron.

If the aqueous solution be boiled a long time with hydrochloric acid, it separates into comenic acid,  $\text{C}_6\text{H}_2\text{O}_5$ , and carbonic acid; the same follows by heating the dry acid to  $200^\circ$ ; at  $250^\circ$  it decomposes into pyromeconic acid,  $\text{C}_{10}\text{H}_3\text{O}_5$ , water, and carbonic acid. *Nitric acid* quickly decomposes meconic acid under production of oxalic and carbonic acid.

If the *nitric acid solution of meconate of silver* be warmed, a violent reaction sets in under production of cyanide of silver, without evolution of nitrous acid. If it be warmed with an excess of potassa solution, it decomposes into carbonic acid, oxalic acid, and a brown material.

The *meconic acid salts* are generally soluble with difficulty and crystallizable; there are neutral and acid salts, which color peroxide of iron salts red.

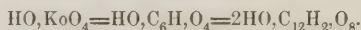
The *potassa salt*,  $\text{KO}, \text{MeO}_6$ , crystallizes in colorless needles of silky lustre; if to the solution more meconic acid be added, thus is the acid salt precipitated.



*Simple Meconate of Lime*:  $\text{CaO}, \text{MeO}_6 + \text{aq.}$  If a solution of simple meconate of lime be brought together with a hot concentrated solution of chloride of calcium, a white precipitate arises.

The *acid lime salt*,  $\text{CaO}, \text{HO}, 2\text{MeO}_6 + \text{aq.}$  crystallizes in prisms; in water soluble with difficulty.

#### KOMENIC ACID:



*Komenic acid* is formed by boiling the aqueous solution of meconic acid with hydrochloric acid. It crystallizes in white grains and warts of stony hardness, which dissolve in 16 parts boiling water and precipitate salts of peroxide of iron with red color. Decomposes at  $150^\circ$  into pyromeconic acid, water, and carbonic acid. Nitric acid decomposes it, under violent action, into carbonic and oxalic acid. It forms with bases neutral and acid salts.

#### PYROMUCIC ACID AND PYROMECONIC ACID.

Both acids have the same constitution, and correspond to the formula  $\text{HO}, \text{C}_{10}\text{H}_3, \text{O}_5$ .

*Pyromucic acid*. *Pyromucic Acid*:  $\text{HO}, \text{pMuO}_5$ . We submit mucic acid to dry distillation, mix the obtained sublimate and distillate with fourfold weight of water, and evaporate the fluid separated from the empyreumatic oils. The obtained pyromucic acid is purified by sublimation. White long leaves; inodorous; of strong acid taste; melts at  $130^\circ$ , and sublimes in white suffocating vapor; soluble in 28 parts cold and 4 parts boiling water. Burns with clear flame. *Nitric acid* has no effect.

The *pyromucic acid salts* have no fixed character. If a hot solution of the acid be saturated with carbonate of lead, we obtain by evaporation brown, transparent, oily drops, which, by degrees, dry to an opaque, white, hard mass.

*Pyromucate of Ethyl*:  $\text{AeOpMuO}_5$ , is obtained when we distil 10 parts pyromucic acid, 20 parts alcohol, and 5 parts concentrated hydrochloric acid, and 4 or 5 times pour back into the retort what has gone over. The last obtained distillate is mixed with water, whereby the ether is precipitated in the form of an oil, which after a few minutes crystallizes in prisms. It is purified by distillation. Colorless, leafy, fatty mass of slight elder odor; of bitter and suffocating taste; melts at  $34^\circ$ ; boils at  $208^\circ$ ; soluble in all proportions in alcohol and ether.

If dry chlorine gas be led into the ether, we obtain a syrup-thick transparent fluid, which is said to contain 1 atom ether and 4 atoms chlorine.

*Pyromeconic Acid*:  $\text{HO}, \text{pMeO}_5 = \text{HO}, \text{C}_{10}\text{H}_3, \text{O}_5 =$  Pyromeconic acid.  
 $\text{HO}, \text{O}_2\text{H}_2\text{O}_2, (\text{C}_6, \text{C}_2\text{H})\text{O}_3$ , is obtained, if meconic or komenic acid be submitted to dry distillation at  $230^\circ$ . Crystallizes from the alcoholic solution in long colorless prisms; melts at  $120$  to  $125^\circ$ ; sublimes without residue; easily soluble in water and alcohol. An extremely weak acid; salts of peroxide of iron impart to the solution a deep-red color; it reduces oxide of silver and gold solution. A drop of potassa solution suffices to impart to the solution of pyromeconic acid an alkaline reaction.

If to an alcoholic solution of the acid *potassa* or *ammonia* be added, thus, by evaporation, the pure pyromeconic acid crystallizes. If hydrate of lime be heated with a solution of the acid, there is deposited from the hot-filtered solution small hard crystals of pyromeconate of lime.

## KINIC ACID:

(Chinic Acid, Chinasäure, G.):  $\text{HO}, \text{ChiO}_{10} = \text{HO}, \text{C}_{14}\text{H}_{10}, \text{O}_{10}$ .

*Kinic acid* is found in cinchona bark in combination with chinin (quinia) and cinchonin (cinchonina). Yellow cinchona bark is extracted with cold water, the organic bases precipitated by lime-water, and the abfiltered fluid evaporated to syrup-thickness. The crystalline paste, which is formed after a few days, is expressed, then dissolved in water, and, by repeated crystallization, pure kinate of lime is procured. This salt is decomposed by sulphuric acid, and the solution, separated from the sulphate of lime, is evaporated. From the aqueous alcoholic solution the acid forms small transparent crystals, which contain 1 atom water of crystallization, which last is lost at  $150^\circ$ ; of strong acid taste; dissolves in  $2\frac{1}{2}$  parts cold water; also soluble in alcohol.

If *kinic acid* be submitted to dry distillation, we obtain phenol, salicylous acid, benzoic acid, hydrobenzid, *hydrochinon* (*vide* page 210), and tar-like substances. Heated with *peroxide of manganese* and *dilute sulphuric acid*, it evolves vapor of chinon. Nitric acid decomposes the acid under production of oxalic acid.

*Kinic acid* is rather strong, and forms *basic* and *neutral salts* soluble in water; mostly crystallizable. The basic lead salt, when exposed to the temperature of  $200^\circ$ , loses 2 atoms water, and then consists of  $2\text{PbO}, \text{C}_{14}\text{H}_8\text{O}_8$ .

*Kinate of potassa* and *ammonia* are deliquescent salts. The *soda salt* crystallizes in needles; the *baryta salt* in *dodecahedrons*. The *potassa salt*,  $\text{CaO}, \text{ChiO}_{10} + 10\text{aq}$ , crystallizes in rhomboidal leaflets, which lose the water of crystallization at  $100^\circ$ ; it dissolves in 6 parts cold water.

*Kinate of Silver*:  $\text{AgO}, \text{ChiO}_{10} + \text{aq}$ , forms white, watery crystals; becoming black in the air.

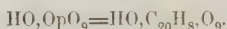
## VERATRIC ACID:



*Veratric acid* is found in the seeds of *Veratrum sabadilla*. The seeds are extracted by alcohol containing sulphuric acid, the obtained extract decomposed by milk of lime, and the alcohol distilled off. The residual fluid is filtered from the deposited veratrin and over-saturated with sulphuric acid. The veratric acid, which is precipitated, is purified by recrystallization from alcohol. Colorless, four-sided columns; reddens litmus; insoluble in ether, soluble in alcohol and boiling water. Cautiously heated upon platinum foil, the crystals volatilize without decomposition. The combinations with the *alkalies* are soluble in water. Acetate of lead and nitrate of silver in the concentrated solution of the ammonia salt, bring forth white precipitates, which vanish upon the addition of water and alcohol.

*Veratrate of Ethyl*:  $\text{AeO, VeO}_7$ , forms a solid, radiated crystalline, inodorous mass; easily pulverizable; readily soluble in alcohol; of bitterish burning taste; sp. gr. 1.141; not volatile, without partial decomposition.

## OPIANIC ACID:



Opianic acid is formed by decomposition of narcotin, and its production is given with that of the latter. It crystallizes in thin, very small prisms; colorless, very voluminous, bitter tasting, and reacting slightly acid. Sparingly soluble in cold water, easily in boiling, as well as in alcohol and ether. It melts at  $140^\circ$ , and, after some time, changes into a white mass insoluble in water, alcohol, and ether. Opianic acid is not volatile. If it be heated to boiling with *superoxide* of lead and water, and then *sulphuric acid*

added in drops, it is converted into *hemipinic acid*  
 Hemipinic acid.  $\text{HO, C}_{10}\text{H}_4\text{O}_5 + 2\text{aq}$ , which crystallizes from the hot aqueous solution in regular, colorless, quadrilateral

prisms; it tastes acid, is soluble with difficulty in water, and easily in alcohol, melts at  $180^\circ$ , sublimes like benzoic acid, and, when warmed with superoxide of lead, sulphuric acid decomposes into carbonic acid and water. If the solution of opianic acid in hot aqueous sulphurous acid be evaporated, there remains the *opian-*

*sulphurous acid*,  $\text{HO, C}_{20}\text{H}_6\text{O}_7, 2\text{SO}_2$ , as a crystalline, inodorous mass, which, brought in contact with water, is again converted partly into opianic acid under evolution of sulphurous acid. If into a solution of opianic acid

warmed to 70° hydrosulphuric acid be several days conducted, and if we then heat the fluid to boiling, the *sulpho-opianic acid* (which has separated as a yellow powder) melts to a pale-yellow clear oil, which stiffens as a transparent, amorphous, sulphur-yellow mass; the unmelted acid crystallizes from the alcoholic solution in fine transparent pale-yellow crystals. Sulph-opianic acid consists of  $\text{HO}, \text{C}_{20}\text{H}_6, \text{O}_7, 2\text{HS}$ . Sulph-opianic acid.

*Opianic Acid Salts.* A hot, saturated, aqueous solution of opianic acid dissolves the carbonates of baryta, lead, and silver, with effervescence, and forms with the bases salts soluble and crystallizable. Ammonia is absorbed by opianic acid under evolution of heat.

If a solution of opianic acid in aqueous ammonia be evaporated, we obtain a transparent amorphous mass; and if this be exposed to the temperature of 100° so long as ammonia is evolved, there remains *opiammon* as a lemon-yellow powder insoluble in water, which consists of  $\text{NC}_{40}\text{H}_{17}\text{O}_{16} = (\text{NH}_3, \text{C}_{20}\text{H}_6\text{O}_7) + \text{C}_{20}\text{H}_8\text{O}_9$ . Opiammon.

If this powder be heated with water to 150° in a glass tube closed by fusion, it decomposes into opianic acid and opianate of ammonia; brought together with caustic alkalies, it does not evolve ammonia until after some time; if the obtained yellow solution be boiled until no more ammonia is evolved, and the hydrochloric acid be added, *xanthopenic acid* is deposited as a lemon-yellow crystalline powder. Xanthopenic.

*Opianate of Ethyl:*  $\text{AeO}, \text{OpO}_9$ , crystallizes in fine fasciculated prisms, which melt at 100°; it decomposes, in contact with alkalies, into alcohol and opianic acid.

*Boletic acid* is found in the juice of *Boletus pseudoignarius*. Crystallizes; colorless; of strong acid taste; sublimable; precipitates the salts of peroxide of iron. Appendix to the acids of this group.

*Fungic acid* is found in many *Fungi*, in *Peziza nigra*, *Hydnum hybridum*, *Boletus juglandis*, etc.; not crystallizable; colorless; strongly acid; easily soluble in water. Acids, whose peculiar nature is yet, in part, doubtful.

*Bebeeruic acid* is found in the bebeeru bark; a white, crystalline, wax-like mass; deliquesces; sublimes in white needles.

*Achilleic acid* is found in the herb of *Achillea millefolium*; crystallizes in quadrilateral, completely colorless prisms; dissolves in 2 parts water; strongly acid; inodorous; non-volatile.

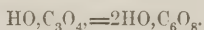
*Krameric acid* is found in the root of *Krameria triandra*; crystallizes; tastes sour; non-volatile, and possesses the remark-



able property of withdrawing sulphuric acid from sulphate of baryta.

*Ignasuric acid* is found in St. Ignatius' beans. *Tobacic acid* in tobacco leaves. *Gnidic acid* in the seed of *Daphne gnidium*. *Solanic acid* in *Solanum nigrum*. *Euphorbic acid* in several species of *Euphorbia*, etc.

#### MESOXALIC ACID:



*Mesoxalic acid* is obtained if the saturated warm solution of alloxanate of baryta (*vide* Uric Acid) be heated to boiling; under evolution of carbonic acid, the mesoxalate of baryta is deposited; it is decomposed in its aqueous solution by sulphuric acid. Crystallizes from its aqueous solution; possesses a very sour taste, and is easily soluble in water.

*Baryta, lime, and silver salts* are precipitated by mesoxalic acid, only when an alkali is present. Nitric acid changes the salts into oxalic acid compounds.

#### MELLITIC ACID:



*Mellitic acid* is found in combination with alumina in mellite (honey-stone), a mineral occurring rarely in strata of brown coal. This mineral is finely ground and treated with a concentrated solution of carbonate of ammonia. We obtain under effervescence acid mellitate of ammonia, and by saturating the solution with ammonia, the neutral salt, which is purified by recrystallization. If we boil the ammonia salt with baryta-water, we obtain mellitate of baryta, and from this, by digesting with sulphuric acid, the pure mellitic acid. Crystallizes from the concentrated solution in needles; easily soluble in water and alcohol; of a sharp acid taste, and durable in the air; the acid burns with a clear, luminous flame under diffusion of an aromatic odor, and is decomposed by either fuming nitric acid or concentrated sulphuric acid.

The *mellitic acid salts* mostly crystallize; there are neutral and acid salts known. The *ammonia salt*,  $\text{NH}_4, \text{O}, \text{C}_4\text{O}_3 + 3\text{aq}$ , crystallizes, and by efflorescence loses 1 atom water. If a solution of mellitate of copper in ammonia be mixed with hydrosulphuric acid, we thus obtain *ter-mellitate of ammonia*.

The *neutral potassa salt*,  $\text{KO}, \text{C}_4\text{O}_3 + 4\text{aq}$ , forms rhombic efflorescing crystals. The *acid potassa salt* appears in large transparent crystals  $= \text{KO}, \text{HO}, 2\text{C}_4\text{O}_3 + 4\text{aq}$ . The *baryta salt* is precipitated by double decomposition as a white mass, which unites in shining crystal scales. The *silver salt*,  $\text{AgO}, \text{C}_4\text{O}_3$ , appears as a fine, crystalline, scaly powder.

*Mellitate of Ethyl* (?). If the boiling alcoholic solution of mellitic acid be evaporated, there remains a gum-like mass which, when water is poured over it, changes into a white, sour-tasting powder.

*Paramid*:  $\text{HO}(\text{NC}_4)\text{C}_4\text{O}_3 = (\text{NH}, \text{C}_4\text{O})\text{C}_4\text{O}_3$ . If mellitate of ammonia be exposed to a temperature of  $150^\circ$ , ammonia is evolved, and a yellowish powder remains, which consists of paramid and euchronate of ammonia. Water withdraws the latter, whilst the former remains.

Paramid is a white, hard, tasteless, and inodorous mass, which, rubbed with water, smells like clay; insoluble in water, alcohol, nitric acid, and nitro-hydrochloric acid itself. If with water it be a long time exposed to the temperature of  $100^\circ$ , a part of it is decomposed under production of acid euchronate and acid mellitate of ammonia. If it be exposed with water to a temperature of  $200^\circ$  in a tube closed by fusion, it is completely converted into acid mellitate of ammonia. If pure ammonia be poured upon it, immediately it becomes yellow, voluminous, and is partially dissolved.

If the solution be immediately brought into hydrochloric acid, a white crystalline body is precipitated, which is named *Paramidic acid*. This consists of  $\text{N}_3\text{C}_{24}\text{H}_5\text{O}_{14} = 2\text{HO}(\text{NH}, \text{C}_4\text{O})\text{C}_4\text{O}_3$ , which is little soluble in hot water, and shows upon zinc the reaction of euchronic acid.

Paramid gives, with oxide of silver, a combination  $= \text{AgO} + (\text{NH}, \text{C}_4\text{O})\text{C}_4\text{O}_3$ . Paramid is decomposed at  $200^\circ$ , under formation of oxalate of ammonia and a sublimate consisting of yellow needles.

*Euchronic Acid*:  $2\text{HO}(\text{NC}_4)\text{C}_4\text{O}_3 + 2\text{aq}$ . Euchronate of ammonia, which is obtained in common with paramid, is dissolved in boiling water, and the solution mixed with hydrochloric acid. During the cooling the euchronic acid is deposited in small four-sided prisms, which contain 2 atoms water. Scarcely soluble in cold water. The aqueous solution of euchronic acid suffers no change from hot hydrochloric and nitric acid. Exposed with water to  $200^\circ$  in a glass tube closed by fusion, it is converted into acid mellitate of ammonia. If a hot solution of euchronic acid be mixed with a dilute solution of acetate of lead microscopic crystals are separated, which consist of  $\text{PbO}, \text{HO}(\text{NC}_4)\text{C}_4\text{O}_3 + 4\text{aq}$ .

The *silver salt* exhibits a sulphur-yellow, heavy powder, and consists of  $2\text{AgO} + (\text{NC}_4)\text{C}_4\text{H}_3 + \text{aq}$ .

If a bright piece of zinc be brought into an aqueous solution of euchronic acid, it is immediately changed into a blue body, *euchron*, which precipitates upon the zinc. If the zinc be dipped a moment in dilute hydrochloric acid,

the euchron is dissolved away, and it then appears as a black mass, which dissolves in ammonia, and in dilute, pure potassa, with a splendid purple color. Euchron is converted by gentle heat immediately into euchronic acid.

### CROCONIC ACID AND RHODIZONIC ACID.

In making potassium (by highly heating charred tartar with coal), with the vapor of potassium there is emitted a black smoke, which is condensed when the emitted gaseous mixture is conducted into several bottles partly filled with naphtha. This black mass is formed by combination of carbonic oxide with potassium. It is supposed that this black body consists of  $K_3 + 7CO$ . If this mass be dissolved in cold alcohol, rhodizonate of potassa remains behind, which, especially by the presence of free potassa, decomposes into croconic acid and oxalate of potassa.

*Croconic Acid:*  $HO, C_5O_4$ . Finely pulverized croconate of potassa is shaken with alcohol, to which not quite so much sulphuric acid is added as is necessary completely to decompose the salt. From the alcoholic solution the croconic acid is obtained in transparent red-yellow, inodorous prisms of astringent, sourish taste, which color the skin deep-yellow, and are soluble in water, alcohol, and ether. If croconate of potassa be treated with *nitric acid*, there remains after evaporation a yellow salt mass. *Chlorine* likewise decomposes the acid. The *croconic acid salts* are in part yellow, part yellowish-red, and part yellowish-brown. The *neutral potassa salt*,  $KO, C_5O_4 + 2aq$ , crystallizes in reddish-yellow, transparent, six or eight-sided prisms; easily soluble in water, insoluble in anhydrous alcohol, neutral; and tastes like nitrate of potassa. The *soda salt* crystallizes in prisms. The *baryta salt* appears as a yellow, insoluble powder; the *copper salt*,  $CuO, C_5O_4 + 3aq$ , crystallizes in small rhombic columns, whose faces possess a lively semi-metallic lustre, and reflect the light with a dark blue color. The powder of the salt is lemon-yellow; heated in the air, it decomposes under emission of sparks. The salt loses at  $100^\circ$  2 atoms of water.

Rhodizonic  
acid.

*Rhodizonic Acid:*  $C_7O_7$  (?). Rhodizonate of potassa, which remains behind when the above-mentioned black mass is completely extracted by alcohol, is diffused in absolute alcohol not completely decomposed by sulphuric acid, and the alcoholic solution evaporated. Appears in pale orange-yellow, fine, short needles, or in brown-black dodecahedrons. Inodorous; tastes astringently sour; reddens litmus, and colors the skin brown-yellow. If the aqueous yellow solution be left a long time in the air, it decomposes into croconic and oxalic acid. Concentrated acid quickly decomposes the acid; an

alkaline solution soon contains croconic and oxalic acid. The *rhodizonic acid salts* most all possess a rose-red to blood-red color; under the polishing brush they assume a remarkable green metallic lustre. Only the potassa salt crystallizes; the most are soluble in water, and all in alcohol. The acid appears to form only basic salts.



## THIRD DIVISION.

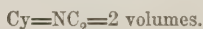
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### AZOCARBYLS.

ONLY two radicals are yet known, which can with certainty be enumerated in the class of the Carbyls, namely, Cyanogen and Mellan. They possess a decided negative character, may be obtained isolated, and are chemically allied to sulphur and selenium as well as to the halogens. However, it may also be assumed that there are radicals consisting of carbon and nitrogen in parabanic and fulminic acid. The constitution of these radicals is then :

Cyanogen, . . . .	Cy = NC <sub>2</sub> ,
Paraban, . . . .	Pr = NC <sub>3</sub> ,
Fulminan, . . . .	Fu = N <sub>2</sub> C <sub>4</sub> ,
Mellan, . . . .	Mll = N <sub>4</sub> C <sub>6</sub> .

### CYANOGEN :



*Cyanogen* is produced : 1. When nitrogen is conducted over an intimate mixture of carbon and potassa ; we obtain cyanide of potassium under evolution of carbonic oxide gas. 2. By the action of ammonia gas upon redhot carbon ; we obtain cyanide of ammonium under evolution of hydrogen gas. All volatile nitrogenous compounds, under co-operation of platinum sponge and a high temperature in contact with hydrocarbons, or if the nitrogenous compound contain hydrogen, with carbonic oxide, leave cyanide of hydrogen and of ammonium. Generally, we obtain cyanogen in combination with the alkali metals, if nitrogenous coal or nitrogenous animal compounds, as dried blood, hoofs, horn, etc., be heated strongly with fixed alkalis ; without doubt, the formation of ammonia takes place here before the formation of cyanogen, and it may be assumed that cyanogen and carbonic oxide are formed by ammonia in contact with excess of carbon and alkali. Formate of ammonia quickly heated, decomposes completely into water and cyanide of hydrogen. 3. By the action of nitric acid upon a

large number of organic compounds; also, if they are non-nitrogenous, we obtain hydrocyanic acid, as upon oil of turpentine, of lemon, of cloves, colophonium, etc., and likewise by distillation of glue with chromate of potassa and dilute sulphuric acid.

Cyanogen appears under ordinary atmospheric pressure as a gasiform body of a peculiar odor, which strongly excites the eyes; burns with a reddish blue flame. One measure of water absorbs  $4\frac{1}{2}$  measures of cyanogen gas, and one measure of alcohol absorbs 23 measures. By a pressure of  $3\frac{1}{2}$  to 4 atmospheres it condenses to a colorless very mobile fluid, whose specific gravity is 0.866 at  $17^{\circ}$ ; the fluid cyanogen is changed under  $-30^{\circ}$  into a radiated ice-like mass, which melts at  $-34^{\circ}$ . We obtain cyanogen by heating cyanide of mercury, or of silver, whereby, however, 1 part is converted into paracyan; or by heating an intimate mixture of 6 parts completely dry ferrocyanide of potassium and 9 parts corrosive sublimate; as residue there remains a mixture of chloride of potassium and cyanide of iron. The gas is received over mercury.

Although cyanogen in some respects is distinguished by great permanency, and in combination with alkali metals bears a very high temperature, yet it is easily decomposed, particularly in contact with water. The affinity between the elements of cyanogen is not great of itself, and its durability in combination with metals in a dry state lies in the negative nature, that is, in the affinity of these compounds. But if the cyanogen comes in contact with water the nitrogen tends with the hydrogen and the carbon with the oxygen, to form compounds of remarkably different chemical characters; and generally, in these circumstances, lies on the other hand, the easy decomposability of cyanogen, a behavior which it exhibits in many cyanogen compounds; it is most always distinguished by great tendency to transposition, whereby very interesting metamerical compounds often arise.—The *aqueous solution* of cyanogen assumes, particularly under the influence of light, little by little, a dark color; it deposits a brownish-black matter consisting of  $N_2C_4H_2O_2$ , which, by heating, decomposes into water and *paracyan*. In the solution are found urea, hydrocyanic acid, carbonate and oxalate of ammonia.

From a solution of cyanogen in *aqueous ammonia*, a brown substance is deposited which consists of *Azulmic Acid*.  $N_2C_3H_2O_2$ , and is called *azulmic acid*, and in the solution are found urea, cyanide of ammonium, carbonate and oxalate of ammonia. Azulmic acid dissolves in alkalies, and is again precipitated upon the addition of acids; it is insoluble in water and alcohol, and at higher temperatures decomposes into paracyan and carbonate of ammonia. In the saturated alkali solution of this acid, salts of the heavy metals produce a brown precipitate.

Paracyan and Paracyanic acid. If cyanide of silver be heated there instantaneously takes place through the whole mass an appearance of light, when half the cyanogen is evolved as gas, and at the same moment the residue is changed into black paracyanide of silver; the same appearance takes place with other cyanides of heavy metals; thus the body which remains behind when Berlin blue is heated to redness, is a mixture of paracyanide of iron and carburet of iron; cyanide of nickel, of cobalt, and of copper, behave in the same manner. The combinations of cyanogen with the alkali metals do not suffer this change. If paracyanide of silver be treated with dilute nitric acid, and the residue dissolved in concentrated sulphuric acid, by diluting with water, the *paracyan*,  $N_4C_8$  (?), is precipitated, which, in a dry state, remains as a loose powder, brownish-black, infusible, non-volatile, soluble in concentrated mineral acids, in pure alkalies, and in the carbonates. If azulmic acid be dissolved in nitric acid and the solution mixed with water, *paracyanic acid*,  $N_4C_8O$  (?), is precipitated, which appears, when dried, as a yellow tasteless powder reddening litmus, and forming with bases acid and neutral salts.

Inorganic compounds which easily yield oxygen, decompose cyanogen in the aqueous solution under production of carbonic acid and separation of nitrogen. *Chlorine* does not act upon dry cyanogen, but if moistness be present we obtain in the sunlight a yellow oil, perhaps a mixture of chloride of carbon and of nitrogen.

#### COMPOUNDS OF CYANOGEN.

Cyanogen behaves, as was observed above, quite like a negative element, and unites with the non-metallic substances and with the metals forming acid, basic, and neutral reacting combinations.

Hydrocyanic acid. *Hydrocyanic Acid*:  $HCy=4$  volumes. Different vegetable substances, as bitter almonds, the kernel of the peach, the apricot, and the cherry, the flowers of the blackthorn, the leaves of the common laurel, the bark of *Prunus padus*, etc., give by distillation with water a distillate containing hydrocyanic acid. These vegetable substances, however, contain no hydrocyanic acid. This acid is first produced by decomposition of amygdalin and similar substances (*see Oil of Bitter Almonds*). Cyanogen and hydrogen do not combine directly, but if they come in contact with each other at the moment of their liberation, hydrocyanic acid is formed. Three parts of dry cyanide of mercury are distilled with two parts fuming hydrochloric acid, and connected with the retort is a tube half filled with pieces of marble, and the other half filled with chloride of calcium, and terminating in a cooled receiver, in which the hydrocyanic acid is condensed; or cyanide of mercury is imperfectly decom-

posed by hydrosulphuric acid, in an apparatus serving the purpose; or we distil three parts of cyanide of potassium with one part concentrated sulphuric acid mixed with an equal weight of water, connecting the retort with a tube bent in the form of a U, partly filled with chloride of calcium, and placed in a vessel of warm water, and also connecting this tube with a bottle placed in ice, for collecting the hydrocyanic acid. We obtain an aqueous solution of hydrocyanic acid when we distil ten parts ferrocyanide of potassium with six parts sulphuric acid and 30 to 40 parts of water, efficiently cooling the receiver, or when we decompose by hydrosulphuric acid, one part of cyanide of mercury dissolved in six parts of water, and then withdraw the excess of hydrosulphuric acid by carbonate of lead. (*Aqua amygdalarum amarum* and *Aqua lauro-cerasi* are distillates containing hydrocyanic acid and oil of bitter almonds).

In an anhydrous condition, a colorless, mobile fluid, of burning taste, and smelling in a dilute state like bitter almonds; sp. gr. at  $7^{\circ}$  = 0.7058, crystallizes at  $-15^{\circ}$  in small needles, boils at  $26.95$ ; soluble in all proportions in water and alcohol of a weak acid reaction; belongs to the most poisonous organic compounds. Conducted through a tube heated to dull redness, it decomposes into equal volumes of cyanogen gas and hydrogen gas. Divides, often even after a few hours, into azulmic acid, which separates, and cyanide of ammonium, and by the presence of water into formate of ammonia. Mixed with an equal volume of *fuming hydrochloric acid*, after a few minutes there arises under evolution of heat, a crystalline mass consisting of chloride of ammonium and formic acid; the same decomposition into formic acid and chloride of ammonium is suffered by the aqueous solution as well as the solution of cyanide of potassium and cyanide of mercury, under co-operation of acids and alkalies. *Chlorine* and *bromine* decompose hydrocyanic acid under production of chloride and bromide of cyanogen. If the gas of anhydrous hydrocyanic acid be conducted over *glowing potassa* or *heated baryta*, we obtain a mixture of cyanide of metal and cyanates under evolution of hydrogen gas. Hydrocyanic acid combines with perchloride of iron, of tin, of antimony, and of titanium, forming crystallizable compounds which decompose in the heat under evolution of hydrocyanic acid. Only potassium and sodium unite directly with cyanogen. The combinations of cyanogen with other metals are obtained 1, by reciprocal decomposition of the metal oxides with hydrocyanic acid; 2, by double elective affinity. The cyanides of the alkali metals in their aqueous solution react acid and act as poisonously as hydrocyanic acid; they are decomposed by all acids under production of hydrocyanic acid. Many cyanides of heavy metals act in like manner, poisonously, but they resist, particularly

Compounds of cyanogen with metals.

A few general behaviors of the same.



cyanide of mercury and cyanide of silver, the action of dilute oxygen acids; but if they are treated with hydrogen acids we obtain hydrocyanic acid and compounds of metals with the halogens, corresponding to those of sulphur. A third class of cyanides of metals, as protocyanide of iron, as well as the compounds of cyanogen, with chromium, cobalt, and manganese, do not act poisonously, and resist the action of acids. But if these compounds be boiled with oxide of mercury and water, we obtain cyanide of mercury and metallic oxide, whence it follows that they, nevertheless, contain unchanged cyanogen. The soluble metallic cyanides give, with salts of the protoxide and peroxide of iron, a whitish or dark-blue precipitate.

The cyanides of metals have a great tendency to unite with each other to form a large series of double compounds. Also these double compounds show some varying properties. Thus cyanide of iron,  $\text{FeCy}$ , combines with two atoms of cyanide of potassium, forming a neutral compound, the ferrocyanide of iron, in which the poisonous properties of cyanide of potassium are completely destroyed. If we mix a concentrated solution of these salts with a concentrated solution of hydrochloric acid, the air being completely excluded, and shake the mixture with some ether, a compound separates which contains one atom  $\text{FeCy}$  to two atoms hydrocyanic acid, but likewise possesses no poisonous properties, reacts strongly acid, and expels oxalic acid itself from its compounds; but if we boil the aqueous solution it decomposes into hydrocyanic acid under separation of protocyanide of iron. The percyanide of iron,  $\text{Fe}_2\text{Cy}_3$ , also behaves like the simple protocyanide; the former combines with  $3\text{KCy}$ , and likewise with  $3\text{HCy}$ . The same relations we observe in respect to percyanide of manganese,  $\text{Mn}_2\text{Cy}_3$ , of chromium,  $\text{Cr}_2\text{Cy}_3$ , of cobalt,  $\text{Co}_2\text{Cy}_3$ . Cyanides of other heavy metals give with cyanide of potassium or of sodium double salts, which still react feebly alkaline, and by dilute acids are immediately decomposed in such a manner that the cyanide of heavy metal is precipitated, whilst that of the alkali is converted into alkali-oxide salt, under production of hydrocyanic acid. Several chemists have determined this difference by which both groups of compounds assume a different constitution; thus the above-mentioned salt of ferrocyanide of iron they regard as consisting of two atoms of potassium, united with a ternary radical  $=\text{N}_3\text{C}_6\text{Fe}$ , and this ternary radical is named ferrocyanogen; the formula of this salt is then  $\text{K}_2 + \text{N}_3\text{C}_6\text{F}$ , and the combination with hydrocyanic acid then consists of  $\text{H}_2 + \text{N}_3\text{C}_6\text{Fe}$ . The compound which percyanide of iron,  $\text{Fe}_2\text{Cy}_3$ , forms with three atoms cyanide of potassium, contains, according to this view, a radical  $=\text{N}_6\text{C}_{12}\text{Fe}_2$ , ferricyanogen, and the constitution of this salt, then, is  $\text{K}_3 + \text{N}_6\text{C}_{12}\text{Fe}_2 = \text{H}_3 + \text{N}_6\text{C}_{12}\text{Fe}_2$ . On the contrary, these chemists assume that the double compound which cyanide

of silver forms with cyanide of potassium, is a real double salt  $=KCy + AgCy$ , because by dilute acids it is immediately separated into cyanide of silver, hydrocyanic acid, and a potassa salt, the first of which is precipitated. But it is farther to be mentioned that the compounds of cyanide of silver with the cyanides of the alkali metals, are decomposed again by chlorides of metals, and likewise by alkalies, and that by decomposition of the combination of the cyanide of silver with cyanide of barium, an acid reacting solution is produced, which forms with alkalies the double compounds mentioned; this solution, must, therefore, contain  $HCy, AgCy$ , whilst, according to the theory above set forth, it must consist of  $H + N_2C_4Ag$ . Generally, one class of cyanides of metals and their double compounds are converted so gradually into the other that no boundary can be fixed, therefore no reason appears for assuming in them a different sort of combination. From all the behavior, however, which, e. g., the salt of the ferrocyanide of iron presents, it most certainly follows that the iron is more intimately united in the compound than the potassium; that potassium can be substituted by other metals and hydrogen; the iron, on the contrary, cannot. If we treat the corresponding lead compound with hydrosulphuric acid, we obtain sulphide of lead and the so-called hydroferrocyanic acid. The protocyanide of iron plays, in all its compounds, the part of a pairling, which forms paired acids with cyanogen and 1, 2, and 3 atoms hydrogen. The formula for hydroferrocyanic acid is hence  $H_2 + (FeCy)^-Cy_2$ , for ferrocyanide of potassium  $K_2 + (FeCy)^-Cy_2$ . This hypothesis, which is assumed in the description of the cyanides of metals, sets no particular radical foremost, still cyanogen is present as such, but in peculiar combination with the pairling whereby its negative property is considerably increased. If the solution of hydroferrocyanic acid be warmed, the pairling is separated; thereby two atoms of cyanogen become free, which unite with 2 atoms hydrogen, forming hydrocyanic acid. Like cyanide of iron, the cyanides of other metals behave in the corresponding compounds; thus cyanide of zinc-potassium consists of  $K + (ZnCy)^-Cy$ , cyanide of silver-potassium of  $K + (AgCy)Cy$ , etc.; in like manner, the formula for the combination of cyanide of mercury, with chloride of potassium, is  $K + (HgCy)^-Cl$ . Of a large number of cyanogen compounds, only a few of the most important can here be mentioned.

*Cyanide of Ammonium*:  $NH_4Cy$ . We submit to gentle sublimation a mixture of equal atoms cyanide of potassium, and chloride of ammonium; colorless, cubical crystals, extremely volatile and poisonous; easily decomposable. *Cyanide of potassium*:  $KCy$ . We heat completely dry ferrocyanide of potassium in an iron crucible, until the cyanogen is completely decomposed, and pour off the fused cyanide of potassium; we then add carbonate of potassa to the ferrocyanide

Simple cyanides of metals.

of potassium; thus we obtain more cyanide of potassium, mixed, however, with cyanate of potassa. It is procured quite pure, if an alcoholic solution of potassa be mixed with a concentrated alcoholic solution of hydrocyanic acid; cyanide of potassium is then deposited. Crystallizes from the aqueous solution in colorless octohedrons; tastes alkaline like bitter almonds, smells like hydrocyanic acid; easily soluble in water; soluble with difficulty in alcohol. In a moist condition it is soon decomposed into ammonia and carbonic acid. Fused cyanide of potassium reduces most metallic oxides under production of cyanate of potash.

*Cyanide of Sodium*:  $\text{NaCy}$ . Like cyanide of potassium; crystallizes with difficulty; easily soluble in water. *Cyanide of barium*,  $\text{BaCy}$ ; soluble with difficulty in water; reacting alkaline. *Cyanide of manganese*,  $\text{MnCy}$ , is obtained by double decomposition; gray-yellow precipitate; insoluble in water; becomes soon brown in the air. *Protocyanide of Iron*:  $\text{FeCy}$ . Freshly precipitated Berlin blue is shaken a few days with hydrosulphuric acid; a white mass, which in the air becomes immediately blue. *Sesquicyanide of iron*,  $\text{Fe}_2\text{Cy}_3 + 3\text{HO}$ , is obtained, if the aqueous solution of hydroferrocyanic acid be boiled some time; a beautiful dark-green powder; insoluble in water and alcohol; is converted at  $230^\circ$  into Berlin blue under loss of cyanogen. *Cyanide of chromium* (sesquicyanide of chromium),  $\text{Cr}_2\text{Cy}_3$ , falls as a light blue-gray precipitate, when a solution of sesquichloride of chromium is dropped into a solution of cyanide of potassium; easily soluble in dilute acid. *Cyanide of cobalt*,  $\text{CoCy} + 3\text{aq}$ . A cinnamon-brown precipitate; it is formed, if hydrocyanic acid be added to a solution of acetate of cobalt. *Sesquicyanide of cobalt*,  $\text{Co}_2\text{Cy}_3$ . Unknown isolated. *Cyanide of nickel*. Light green powder; loses its water at  $180^\circ$ , and becomes brown. *Cyanide of zinc*,  $\text{ZnCy}$ . White powder; is obtained like cyanide of cobalt. *Cyanide of cadmium*,  $\text{CdCy}$ , is obtained by dissolving freshly precipitated hydrate of oxide of cadmium in hydrocyanic acid; white crystals; unchangeable in the air. *Cyanide of lead*,  $\text{PbCy}$ . White, insoluble powder. *Dicyanide of copper*. We treat hydrate of protoxide of copper with aqueous hydrocyanic acid; white powder; soluble in ammonia. *Protocyanide of copper*,  $\text{CuCy}$ . A mutable combination, which is insoluble in water, and is obtained by digestion of oxyhydrate of copper with hydrocyanic acid. Decomposes under evolution of cyanogen into a compound  $= \text{Cu}_2\text{Cy} + \text{CuCy} + 5\text{aq}$ , which is obtained in small very shining crystals. *Cyanide of mercury*,  $\text{HgCy}$ . We dissolve oxide of mercury in aqueous hydrocyanic acid, or we boil 2 parts Berlin blue with 1 part oxide of mercury. Crystallizes in right-angled four-sided prisms; easily soluble in boiling water, soluble with difficulty in alcohol; very poisonous; soluble in nitric acid. *Cyanide of silver*,  $\text{AgCy}$ . White powder; insoluble in water and dilute acids. Is completely precipitated if hydrocyanic acid be added to a solution of nitrate of silver. *Cyanide of platinum*,



PtCy, remains behind as a beautiful greenish-yellow powder, if cyanide of platinum-mercury be heated in a retort; insoluble in alkalis, water, and alcohol. *Protocyanide of gold*, AuCy. A solution of cyanide of potassium-gold is evaporated to dryness with hydrochloric acid, and the residue treated with water. Beautiful yellow, crystalline, and tasteless powder; insoluble in water, alcohol, and ether, and not attacked by the strongest acids. *Tercyanide of gold*, AuCy<sub>3</sub>+6aq. If cyanide of silver-gold, obtained by precipitation of cyanide of potassium-gold with nitrate of silver, be treated with hydrochloric acid, we obtain chloride of silver and a solution of tercyanide of gold, which, by spontaneous evaporation, remains behind in large leaves; unchangeable in the air, and soluble in all proportions in water, alcohol, and ether. Oxalic acid itself does not, by continued boiling, effect any reduction.

*Cyanide of Potassium-manganese*: K<sub>3</sub>+(Mn<sub>2</sub>Cy<sub>3</sub>)<sup>-</sup>Cy<sub>3</sub>, is obtained under deposition of oxyhydrate of manganese, if a solution of cyanide of manganese in cyanide of potassium be gently evaporated. Small brown-red crystals; soluble in water. The solution of this salt gives with salt of protoxide of iron a blue precipitate, with salts of protoxide of manganese a reddish-yellow, with salts of deutoxide of copper a green, with salts of protoxide of lead a brown, and with nitrate of silver a yellowish-green precipitate.

Double compounds of cyano-  
gen.  
Paired compounds.

## COMPOUNDS OF FERROCYANOGEN.

*Hydroferrocyanic Acid*: H<sub>2</sub>+(FeCy)<sup>-</sup>Cy<sub>2</sub>. A concentrated solution of ferrocyanide of potassium free of air, and mixed with excess of hydrochloric acid, is shaken with ether, whereby hydroferrocyanic acid is precipitated. Crystallizes from the alcoholic solution in dazzling white pearly leaflets. Easily soluble in water and alcohol, and precipitable from its solution by ether; taste very sour. If the solution be boiled, it is decomposed into hydrocyanic acid and protocyanide of iron. The same decomposition also takes place by heating the dry acid.

Combinations of  
simple cyanide  
of iron.

*Ferrocyanide of Ammonium*: 2NH<sub>4</sub>+(FeCy)<sup>-</sup>Cy<sub>2</sub>, is obtained by saturating the preceding compound with ammonia. Crystallizes in shining straw-yellow, regular octohedrons. By heating the aqueous solution cyanide of ammonium is evolved under separation of protocyanide of iron. Gives crystallizable compounds with *chloride and bromide of ammonium*.

*Ferrocyanide of Potassium*: K<sub>2</sub>+(FeCy)<sup>-</sup>Cy<sub>2</sub>+3aq. Into a hot solution of potassa we bring finely pulverized Berlin blue until the color no longer vanishes, and evaporate the solution separated from the oxyhydrate of iron. (Made in large quantities: 1st, by heating nitrogenous coal to redness with potassa and iron, and 2dly, by direct heating of animal substances with potash.) Crystallizes in large wine-yellow right-angled tables; tastes bitter



and briny; loses in vacuum 3 atoms of water; dissolves in 4 parts cold water, and in 2 parts of boiling; insoluble in alcohol. By glowing decomposes into a mixture of carburet of iron and cyanide of potassium. Gives, by digestion with oxide of mercury, cyanide of mercury, potassa, and peroxide of iron.

If 2 atoms of ferrocyanide of potassium be treated with 5 atoms of ordinary *nitric acid* under strong refrigeration, we obtain, under evolution of cyanogen gas, hydrocyanic acid, azote, and carbonic acid, and also a coffee-brown solution, in which are found later nitrate of potash, oxamid, ferricyanide of potassium, and nitroferrocyanide of potassium,  $K_2 + (Fe_2Cy_3NO_2)^-Cy_2$ . If to a solution of ferrocyanide of potassium a solution of metal salts be added, we generally obtain precipitates, in which  $K_2$  in ferrocyanide of potassium is replaced by 2 atoms of metal. As these precipitates have different colors, we frequently use ferrocyanide of potassium as a reagent upon metals. Yet these precipitates often appear to contain some potassium. Alkali salts as well as earth salts are not precipitated; gold and platinum give no corresponding compounds.

*Ferrocyanide of Sodium*:  $Na_2 + (FeCy)^-Cy_2 + 12aq$ . Crystallizes in quadrilateral prisms, effloresces in the air, dissolves in  $4\frac{1}{2}$  parts of water. *Ferrocyanide of barium*,  $Ba_2 + (FeCy)^-Cy_2 + 6aq$ ; small, yellow quadrilateral prisms; soluble in 100 parts boiling water and in 1900 parts cold. *Ferrocyanide of potassium-barium*,  $KBa + (FeCy)^-Cy_2$ ; crystallizes in shining lemon-yellow prisms; soluble in 36 parts water; is obtained if a solution of ferrocyanide of potassium be mixed with a solution of ferrocyanide of barium. *Ferrocyanide of potassium-manganese*,  $KMn + (FeCy)^-Cy_2$ , is precipitated if sulphate of protoxide of manganese be brought by drops into a solution of ferrocyanide of potassium; after the drying, a blue powder is exhibited. *Ferrocyanide of iron*,  $Fe_2 + (FeCy)^-Cy_2$ , appears not to exist. If to a solution of ferrocyanide of potassium, we add a salt of protoxide of iron, thus is formed a white precipitate, which consists of  $(KFe + [FeCy]Cy_2) + (Fe_2 + [FeCy]Cy_2)$ . *Ferrocyanide of potassium-iron*,  $KFe + (FeCy)Cy_2$ , is deposited as a white powder, if ferrocyanide of potassium be distilled with dilute sulphuric acid, under production of hydrocyanic acid. *Ferrocyanide of cobalt*,  $Co_2 + (FeCy)^-Cy_2$ . Ferrocyanide of potassium produces a greenish precipitate in the salts of peroxide of cobalt. *Ferrocyanide of zinc*,  $Zn_2 + (FeCy)^-Cy_2$ . Hydroferrocyanic acid produces a white precipitate in zinc salts. *Ferrocyanide of potassium-zinc*,  $KZn + (FeCy)^-Cy_2$ , is white, and is precipitated if sulphate of zinc be brought together with ferrocyanide of potassium. *Ferrocyanide of lead*,  $Pb_2 + (FeCy)^-Cy_2$ ; white, insoluble powder. *Ferrocyanide of copper*,  $Cu_2 + (FeCy)^-Cy_2$ . Ferrocyanide of potassium produces a brown precipitate in the copper salts. If a solution of a copper salt be brought by drops into a solution of ferrocyanide of potas-

sium the brown precipitate soon becomes red and consists of  $\text{KCu} + (\text{FeCy})^-\text{Cy}_2$ . *Ferrocyanide of silver*,  $\text{Ag}_2 + (\text{FeCy})^-\text{Cy}_2$ , appears as a white precipitate. *Ferrocyanide of molybdenum*,  $\text{Mo}_2 + (\text{FeCy})\text{Cy}_2$ . Salts of molybdenum give a dark-brown precipitate with ferrocyanide of potassium.

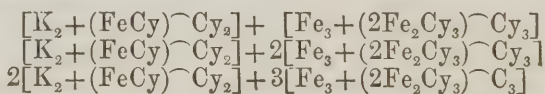
*Hydroferricyanic Acid*:  $\text{H}_3 + (\text{Fe}_2\text{Cy}_3)^-\text{Cy}_3$ . Ferricyanide of lead, diffused in water, is decomposed by hydrosulphuric acid, and the solution evaporated in a vacuum. Reddish-yellow acid-tasting crystals, soluble in water and alcohol; decomposes in the air under deposition of a blue crystalline precipitate. Compounds of sesquicyanide of iron.

*Ferricyanide of Potassium*:  $\text{K}_3 + (\text{Fe}_2\text{Cy}_3)^-\text{Cy}_3$ . We conduct chlorine into a dilute solution of ferrocyanide of potassium until a test no longer precipitates peroxide of iron blue; or, we digest Berlin blue with hypochlorite of potassa. Crystallizes in beautiful, large, ruby-red, direct rhombic columns. If the solution be treated with hydrosulphuric acid, we obtain hydrocyanic acid and ferrocyanide of potassium under deposition of sulphur. Ferricyanide of potassium is, in combination with pure potassa, a powerful oxidizing body, because it is converted into ferrocyanide of potassium, the cyanogen, which is set free, combining with the potassium and the liberated oxygen, oxidizing other bodies; thus protoxide of manganese is converted into superoxide; in like manner, the oxides of nickel, cobalt, tin, and lead, more highly oxidize. If a solution of oxide of chromium in potassa be mixed with the salt, we obtain chromate of potassa. Ferricyanide of potassium, like ferrocyanide of potassium, gives, with the salts of heavy metals, different colored precipitates, in which  $\text{K}_3$  is replaced by  $\text{M}_3$ . *Ferricyanide of sodium*,  $\text{Na}_3 + (\text{Fe}_2\text{Cy}_3)^-\text{Cy}_3$ , forms ruby-red, tabular crystals, easily soluble in water. *Ferricyanide of barium* is obtained by dissolving carbonate of baryta in hydroferricyanic acid. *Ferricyanide of potassium-barium*,  $\text{KBa}_2 + (\text{Fe}_2\text{Cy}_3)^-\text{Cy}_3 + \text{Ga}_2$ , is obtained by the action of chlorine upon ferrocyanide of potassium-barium. Almost black six-sided columns.

If to a solution of peroxide of iron salts we add a solution of ferrocyanide of potassium, or ferricyanide of potassium to protoxide of iron salts, blue precipitates are formed, which, however, according as one or the other substance is applied in excess, are very differently constituted, and very often still contain potassium. The combinations, at present known, correspond to the following formulæ:— Behavior of ferrocyanide of potassium to salts of peroxide of iron and of ferricyanide of potassium to salts of protoxide of iron.

First combination	. . . .	$\text{Fe} + (\text{Fe}_2\text{Cy}_3)^-\text{Cy} + 4\text{aq.}$
Second	“ . . . .	$\text{Fe} + (2\text{Fe}_2\text{Cy}_3)^-\text{Cy} + 5\text{aq.}$
Third	“ . . . .	$\text{Fe}_3 + (\text{Fe}_3\text{Cy}_3)^-\text{Cy} + 13\text{aq.}$
Fourth	“ (Berlin blue)	$\text{Fe}_3 + (2\text{Fe}_2\text{Cy}_3)^-\text{Cy}_3$
Fifth	“ . . . .	$\text{Fe}_3 + (2\text{Fe}_2\text{Cy}_3)^-\text{Cy}_3 + \text{Fe}_2\text{O}_3.$

*Fourth Compound, Berlin Blue (Paris Blue):*  $\text{Fe}_3 + (2\text{Fe}_2\text{Cy}_3)\text{Cy}_3$   $\text{Cy}_3 = 3\text{FeCy} + 2\text{Fe}_2\text{Cy}_3$ . If to a boiling solution of ferricyanide of potassium we add a quantity of protoxide of iron salt not sufficient for decomposition, or if we precipitate salts of peroxide of iron with hydroferrocyanic acid, thus is precipitated pure Berlin blue, and in the former case the solution contains ferrocyanide of potassium:  $2[\text{K}_3 + (\text{Fe}_2\text{Cy}_3)\text{Cy}_3] + 4\text{FeO} = [\text{Fe}_3 + (2\text{Fe}_2\text{Cy}_3)\text{Cy}_3] + [\text{K}_2 + (\text{FeCy})\text{Cy}_2] + 4\text{KO}$ . The Berlin blue thus obtained, when dried at  $40^\circ$ , contains yet 20 atoms of water. Generally, Berlin blue is obtained when a solution of a salt of peroxide of iron is precipitated by ferrocyanide of potassium in such a manner, under continued stirring, that the peroxide of iron salts remain in excess. The most beautiful blue is obtained by the employment of nitrate of peroxide of iron. Berlin blue, dried by ordinary temperature, exhibits a light, not crystalline dark-blue body; possesses a copper-red streak, is insoluble in acids, and, at high temperature, decomposes into water, hydrocyanate and carbonate of ammonia. In the sunlight it is bleached under loss of cyanogen. It is decomposed by *chlorine water* and *nitric acid*. *Concentrated sulphuric acid* changes it into a white gelatinous mass. *Pure alkalis* form ferrocyanide of potassium under deposition of peroxide of iron. If it be boiled with deutoxide of mercury, we obtain cyanide of mercury. Berlin blue dissolves in oxalic acid (6 parts blue, 1 part acid, and 10 parts water) with a beautiful blue color (blue ink). Berlin blue combines with ferrocyanide of potassium in several proportions; these compounds correspond to the following formulæ:—



*Fifth Combination. Basic Berlin Blue:*  $[\text{Fe}_3 + (2\text{Fe}_2\text{Cy}_3)\text{Cy}_3] + \text{Fe}_2\text{O}_3$ , is obtained, if into a solution of ferrocyanide of potassium a solution of salts of protoxide of iron be cautiously brought, so that a part of the former remains undecomposed; a white precipitate is formed, which probably consists of  $(\text{KFe}_2)\text{Cy}_3 + 3\text{FeCy}$ , and in the air becomes blue under production of peroxide of iron. Chlorine converts the white body immediately into Berlin blue.

*Combinations of Ferrocyanide of Potassium with Berlin Blue.*

1. *Turnbull's Blue:*  $[\text{KFe} + (\text{FeCy})\text{Cy}_2] + [\text{Fe}_3 + (2\text{Fe}_2\text{Cy}_3)\text{Cy}_3]$ . Is obtained, if a solution of ferricyanide of potassium, under continued stirring, be mixed with a solution of sulphate of protoxide of iron whose quantity is not sufficient for the complete decomposition of the ferricyanide. A remarkably beautiful blue,



finely divided precipitate. 2. If we add a solution of a salt of peroxide of iron to a solution of ferrocyanide of potassium (but not the reverse) there is formed a blue precipitate which, after complete washing, partly dissolves in water. After evaporation of the solution, a dark blue mass, which consists of 1 atom of ferrocyanide of potassium and 1 atom Berlin blue, and is called *soluble Berlin blue*. The insoluble part is a compound of 1 atom of ferrocyanide of potassium with 2 atoms of Berlin blue.

*Ferricyanide of Copper*:  $\text{Cu}_3 + (\text{Fe}_2\text{Cy}_3)^-\text{Cy}_3$ . Ferricyanide of potassium produces in a salt of peroxide of copper a dirty yellow precipitate.

## NITROFERRICYANOGEN COMPOUNDS.

(Nitroprussidverbindungen, G.)

*Nitroferricyanhydric Acid*:  $\text{H}_2 + (\text{Fe}_2\text{Cy}_3, \text{NO}_2)\text{Cy}_2$ , Nitroferricyanogen compounds.  
is obtained if the silver compound be decomposed by hydrochloric acid. Evaporated in a vacuum, we obtain dark-red deliquescent crystals; soluble in water, alcohol, and ether. *Nitroferricyanide of potassium*:  $\text{K}_2 + (\text{Fe}_2\text{Cy}_3, \text{NO}_2)\text{Cy}_2$ . The coffee-brown fluid obtained by dissolving ferrocyanide of potassium in nitric acid (*vide* Ferrocyanide of Potassium) is digested upon the water-bath, until the salt of peroxide of iron is no longer precipitated blue, but of slate color; is afterwards strongly refrigerated; thus separates much nitrate of potassa, and often oxamid also. We saturate the mother-liquor in the cold with carbonate of potassa, then heat to boiling, filter off the existing brown precipitate, and obtain, after evaporation, crystals of nitroferricyanide of potassium, which dissolve in equal parts of water. *Nitroferricyanide of sodium*,  $\text{Na}_2 + (\text{Fe}_2\text{Cy}_3, \text{NO}_2)^-\text{Cy}_2$ , we obtain in like manner; ruby-red crystals resembling ferricyanide of potassium.

*Nitroferricyanide of Barium* is obtained by decomposition of the copper salt by baryta-water; crystallizes in dark-red quadrangular columns; easily soluble. The *copper compound* is obtained if the potassium compound be mixed with sulphate of copper; is not soluble in water; pale-green. If the soluble compound be treated with caustic alkalies in boiling heat, it decomposes into nitrogen, peroxide of iron, ferrocyanide of potassium and nitrites. If we bring a solution of it together with the slightest quantity of an alkaline sulphide, there is immediately formed a splendid purple-red or blue color. In the aqueous solution this color soon disappears, but if an alcoholic solution be employed, the purple-colored compound is precipitated in oily drops, which dry in a vacuum to a green powder; it contains sulphide of an alkali metal.



Compounds of sesquicyanide of chromium. *Hydrochromecyanic Acid*:  $H_3 + (Cr_2Cy_3)^-Cy_3$ . We decompose cyanide of lead-chromium with hydrosulphuric acid. Crystallizes; is very acid; decomposes, by boiling the aqueous solution, into hydrocyanic acid and cyanide of chromium.

*Chromecyanide of Potassium*:  $K_3 + (Cr_2Cy_3)^-Cy_3$ , forms vinous-yellow crystals. The aqueous solution gives, with *acetate of lead*, a white precipitate and with nitrate of silver a yellow one.

Compounds of cyanide of cobalt. *Hydrocobaltcyanic Acid*:  $H_3 + (Co_2Cy_3)^-Cy_3$ . Colorless, fibrous crystals; of strong acid taste, and easily soluble in water. *Cyanide of potassium-cobalt*,  $K_3 + (Co_2Cy_3)Cy_3$ . Crystallizes in pale-yellow four-sided prisms. The solution precipitates rose-red salts of oxide of cobalt.

Compounds of cyanide of nickel. *Nickeleyanide of Potassium*:  $K + (NiCy)^-Cy + aq$ , crystallizes in honey-yellow rhombic columns. The solution of the salt gives with the salts of the heavy metals different colored precipitates, in which one atom of potassium is replaced by one atom of metal. *Nickelcyanide of sodium*,  $Na + (NiCy)^-Cy + 5aq$ , crystallizes in transparent prisms. Boiled with hydrochloric acid, we obtain chloride of potassium and of nickel.

Compounds of cyanide of zinc. *Zincecyanide of Potassium*:  $K + (ZnCy)^-Cy$ , is obtained by dissolving cyanide of zinc in cyanide of potassium. Crystallizes in large, colorless octohedrons. Gives, by boiling with hydrochloric acid, chloride of zinc. *Zincecyanide of barium*,  $BaZn + (ZnCy)^-Cy_2$ , is precipitated as a soluble powder, if to the solution of potassa salt acetate of baryta be added. *Zincecyanide of lead*,  $ZnPb + (ZnCy)^-Cy_2$ , appears as a white powder.

Compounds of cyanide of mercury. *Mercurycyanide of Potassium*:  $K + (HgCy)^-Cy$ . Crystallizes in white transparent octohedrons; likewise the *sodium compound*, the *barium*, the *calcium*, and the *magnesium compound*. Cyanide of mercury forms, farther, with *chlorides*, *bromides*, and *iodides of metals*, a series of double compounds, which all crystallize. Also are combinations known with *chromate* and *formate of potassa*.

Compounds of cyanide of silver. *Hydrosilvercyanic Acid*:  $H + (AgCy)^-Cy$ , is known only in aqueous solution; is obtained by precipitation of silvercyanide of barium by sulphuric acid. *Silvercyanide of potassium*,  $K + (AgCy)Cy$ , crystallizes in octohedrons. If the solution of this salt be brought together with the salts of heavy metals, compounds are thus obtained, which consist of  $M + (AgCy)^-Cy$ .

Compounds of protocyanide of platinum. *Hydroplatincyanic Acid*:  $H + (PtCy)^-Cy$ , is obtained by decomposition of the mercury compound by hydrosulphuric acid. Greenish-yellow substance; soluble in water and alcohol, of metallic sour taste.

Crystallizes from the concentrated solution in beautiful stellar-groups of needles, which possess a metallic gold lustre. Decomposes above  $100^{\circ}$  into hydrocyanic acid and cyanide of platinum. *Platincy anide of potassium*,  $K + (PtCy)^{-}Cy + 3aq$ , is obtained if a solution of bichloride of platinum be boiled with cyanide of potassium. Crystallizes in long, thin, rhombic columns, which appear yellow by transmitted light and blue by reflected. If to a solution of this salt be added a solution of *chloride of zinc*, or of *cobalt*, of *nitrate of copper*, or *carbonate of silver* in ammonia, thus is obtained a crystallizable combination, which consists of  $M + (PtCy)^{-}Cy + NH_3$ . *Platinumcyanide of mercury*,  $Hg + (PtCy)^{-}Cy$ , is obtained if nitrate of protoxide of mercury be added to a solution of potassium salt, and the obtained precipitate boiled with dilute nitric acid. A white body, which by heating decomposes into mercury, cyanogen, and cyanide of platinum.

*Platinumcyanide of Potassium* (Platinum-sesquicyanide of Potassium):  $K_2 + (Pt_2Cy_3)^{-}Cy_2 + 5aq$ , is obtained, if chlorine gas be conducted into a solution of platinumcyanide of potassium. Separates from the hot aqueous solution in perfect copper-red prisms of metallic lustre. Easily soluble in water, insoluble in alcohol. Decomposes by heating under evolution of cyanogen. The aqueous solution gives, with *copper salts*, a greenish-white precipitate, with *salts of silver* and *mercury*, a white one. *Bicyanide of platinum*,  $PtCy_2$ , gives, with chloride of potassium, a compound which crystallizes in large rhomboidal tables, and consists of  $KCl + PtCy_2 + 2aq$ . Is obtained if platinumcyanide of potassium,  $K_2 + (Pt_2Cy_3)^{-}Cy_2$ , be dissolved in hot dilute nitrohydrochloric acid.

Compounds of the platinum-cyanide.

*Aurocyanide of Potassium*:  $K + (AuCy)^{-}Cy$ . We dissolve fulminating gold (obtained by precipitation of chloride of gold with ammonia) in a concentrated hot solution of cyanide of potassium. By cooling the salt separates in colorless prismatic crystals, often an inch long. If the solution be mixed with nitrate of silver, a white precipitate is formed  $= Ag + (AuCy)^{-}Cy$ .

Compounds of protocyanide of gold.  $AuCy$ .

*Auricyanide of Potassium*:  $K + (AuCy_3)^{-}Cy + 1\frac{1}{2}aq$ . A solution of neutral chloride of gold is brought into a hot concentrated solution of cyanide of potassium. Crystallizes, during the cooling, in beautiful large tabular crystals; decomposes, by excluded air, into cyanogen and aurocyanide of potassium. Gives, with nitrate of silver, a cheesy precipitate  $= Ag + (AuCy_3)^{-}Cy$ .

Compounds of sesquicyanide of gold.  $AuCy_3$ .

*Cyanic Acid*:  $CyO$ . If cyanide of potassium be heated with peroxide of manganese, protoxide and peroxide of lead, etc., cyanate of potassa is obtained. The acid is not known in anhydrous condition; if it comes in contact with water it is immediately decom-

Cyanogen and oxygen. Cyanic acid.

posed into carbonic acid and ammonia:  $\text{NC}_2\text{O} + 3\text{HO} = 2\text{CO}_2 + \text{NH}_3$ .

*Cyanic acid.* *Hydrate of Cyanic Acid:*  $\text{HO}, \text{CyO}$ , is obtained, if the hydrate of cyanurenic acid  $= 2\text{HO}, \text{N}_3\text{C}_6\text{HO}_4$ , be heated to glowing, in a small retort with long neck, and the distillate collected in a receiver bound in snow and salt;  $2\text{HO}, \text{N}_3\text{C}_6\text{HO}_4 = 3(\text{HO}, \text{NC}_2\text{O})$ . Below  $0^\circ$  the hydrate appears as a colorless, volatile, thin-flowing liquid of suffocating, acid, extremely penetrating odor. The smell of the vapor powerfully excites tears; the smallest drop brought upon the skin produces a blister. If the gaseous acid be conducted into ice, we obtain an aqueous solution of the former, but which is soon decomposed. If the fluid acid be exposed to the temperature of  $0^\circ$ , it commences boiling, and changes, under violent explosions, into a snow-white inodorous mass, which is named *oxide of uren*, and consists of  $\text{NC}_2\text{HO}_2$ . *Hydrate of cyanic acid and water* change into carbonic acid and ammonia. If the vapor of cyanic acid be conducted into alcohol, we obtain *allophanate of ethyl*  $= \text{AeO}, \text{N}_2\text{C}_4\text{H}_3\text{O}_5$ ; if the hydrate comes together with aldehyd, there is produced *trigenic acid*,  $\text{HO}, \text{N}_3\text{C}_8\text{H}_7\text{O}_4$ , and brought together with aqueous ammonia, it forms *urea*  $\text{N}_2\text{C}_2\text{H}_4\text{O}_2$ . By the action of the vapor of cyanic acid upon *amyl spirit cyanurenic acid*,  $2\text{HO}, \text{N}_3\text{C}_6\text{HO}_6$ , arises. If *hydrochloric acid* gas be conducted over *cyanate of silver*, we obtain a fluid combination which may be considered as consisting of  $\text{HCl}, \text{HO}, \text{CyO}$ ; this compound is decomposed by ordinary temperature, and becomes solid under evolution of hydrochloric and carbonic acid, and formation of chloride of ammonium, and oxide of uren.

*Cyaniates.* The alkali salts can be heated to glowing without suffering decomposition; dissolved in water, they divide into double carbonates under evolution of ammonia. If acid is poured upon the dry salts, carbonic acid is evolved. The *ammonia salt*,  $\text{NH}_4\text{O} + \text{CyO}$ , is known only in aqueous solution; by evaporation it is changed into urea. The *potassa salt*,  $\text{KO}, \text{CyO}$ , is best obtained, if by gentle heat we fuse 8 parts ferrocyanide of potassium and 3 parts of carbonate of potassa, adding, by degrees, 15 parts protoxide of lead, and pouring off the cyanate of potassa. Crystallizes from the alcoholic solution in thin, transparent leaflets, tastes like nitrate of potassa, is easily soluble in water, and scarcely soluble in anhydrous alcohol. If to the concentrated solution some acid be added, cyanate of potassa is deposited. If it be fused with potassium, we obtain cyanide of potassium and potassa. The *baryta salt*,  $\text{BaO}, \text{CyO}$ , is obtained in small prisms, if a solution of cyanate of potassa be mixed with acetate of baryta and then with alcohol. The *silver salt*,  $\text{AgO}, \text{CyO}$ , is obtained by double decomposition, as a white precipitate which dissolves in ammonia; from the solution, by evaporation, we obtain



large crystals, which consist of cyanate of silver and ammonia. Gives, by heating, dicyanide of silver,  $\text{Ag}_2\text{Cy}$ .

*Cyanate of Methyl*:  $\text{MeO.CyO}$ . If cyanate of potassa be distilled with methyloxyd-sulphate of potassa, we obtain a mixture of cyanate and cyanurate of methyl. The former is very volatile, and can be removed from the latter by distillation; fluid, and gives with ammonia a crystallizable compound, which consists of  $\text{N}_2\text{C}_4\text{H}_6\text{O}_2$ , and is named *acetyl-urea*. *Cyanate of ethyl*,  $\text{AeO.CyO}$ , is obtained in like manner. Very mobile fluid, strongly refracting light, not so heavy as water; the vapor strongly excites to tears. Gives, with ammonia, a body crystallizing in prisms,  $=\text{N}_2\text{C}_6\text{H}_8\text{O}_2$ , the so-called *metacetyl-urea*. If cyanate of methyl be treated with water, we obtain, under evolution of carbonic acid, a crystallizable body of the same constitution. *Cyanate of amyl*,  $\text{AmO.CyO}$ , is, in like manner, produced. Fluid, boils at  $100^\circ$ , and gives with ammonia a combination  $=\text{N}_2\text{C}_{12}\text{H}_{14}\text{O}_2$ , or the *amyl-urea*.

Acetyl-urea, . . . .  $(\text{N}_2\text{C}_2\text{H}_4\text{O}_2) + \text{C}_2\text{H}_2$ .

Metacetyl-urea, . . . .  $(\text{N}_2\text{C}_2\text{H}_4\text{O}_2) + 2\text{C}_2\text{H}_2$ .

Amyl-urea, . . . .  $(\text{N}_2\text{C}_2\text{H}_4\text{O}_2) + 5\text{C}_2\text{H}_2$ .

(Compare Urea.)

If *cyanide of potassium* be melted together with sulphur by gentle heat, and the melted mass dissolved in water, thus are obtained after evaporation crystals, which consist of  $\text{K} + \text{NC}_2\text{S}_2$ ; and if these crystals are distilled with phosphoric acid, there goes over the so-called hydrosulphocyanic acid,  $\text{H} + \text{NC}_2\text{S}_2$ . If we let this acid act upon metallic oxides, thus are obtained, under formation of water, metal compounds, which consist of  $\text{M} + \text{NC}_2\text{S}_2$ ; hydrosulphuric acid decomposes these compounds under production of sulphide of metal and hydrosulphocyanic acid. Hence it follows that hydrosulphocyanic acid cannot correspond to the formula  $\text{HS} + \text{CyS}$ , but is to be considered as a hydrogen acid of a sulphur-containing radical. Besides the hydrosulphocyanic acid, still the hydrobisulphocyanic acid is known, which consists of  $\text{H} + \text{NC}_2\text{S}_3$ . If we assume in the compound a sulphur-holding radical then the formulæ are:—

Cyanogen and sulphur.

Hydrosulphocyanic acid,  $\text{H} + (\text{NC}_2\text{S}_2) = \text{Hydrorhodanic acid}$ ,  
Hydrobisulphocyanic “  $\text{H} + (\text{NC}_2\text{S}_3) = \text{Hydroxanthanic acid}$ .

These compounds, however, can also be compared with hydroferrocyanic and hydroplatinumcyanic acid. They then contain cyapide of sulphur paired with sulphur, and their formulæ are:—

Hydrosulphocyanic acid, . .  $\text{H} + (\text{CyS})^{\wedge}\text{S}$ ,  
Hydrobisulphocyanic “ . .  $\text{H} + (\text{CyS}_2)^{\wedge}\text{S}$ .



The latter view is adopted below.

*Hydrosulphocyanic Acid*:  $H + (CyS)^{\wedge}S$ . It is found in mustard-seed, and in the saliva of men and of sheep. The anhydrous acid is obtained if sulphocyanide of mercury be decomposed by hydrosulphuric acid. We obtain oily drops, which immediately stiffen crystalline. The anhydrous acid quickly decomposes into hydrobisulphocyanic acid under evolution of hydrocyanic acid. If we distil a concentrated solution of sulphocyanide of potassium with concentrated phosphoric acid, we thus obtain hydrous acid of very sour taste and suffocating odor; possesses the specific gravity of 1.022; boils at  $103^{\circ}$ , and crystallizes at  $-14^{\circ}$ . The solution of the acid colors the most dilute solution of peroxide of iron salts blood-red. The products, which are formed by the action of *nitric acid* and *chlorine* upon sulphocyanide of potassium and hydrosulphocyanic acid are described at *uren*; likewise the products, which are obtained by heating *sulphocyanide of ammonium*.

*Sulphocyanides of Metals* (Rhodanmetalle). We obtain sulphocyanides of metals: 1st, by treating the metallic oxide with aqueous sulphohydrocyanic acid; 2dly, if cyanide of an alkali metal be fused together with sulphur; 3dly, if cyanogen gas be conducted over the higher sulphur compounds of the alkali metals in glowing heat; the insoluble are obtained by double decomposition. The sulphocyanides of the alkali metals suffer no decomposition even in the glowing heat. The heavy metal compounds, by glowing in a closed vessel, generally give nitrogen, sulphocarbonic acid, and cyanogen gas, whilst sulphides of metal remain behind. The soluble compounds give, with peroxide of iron, a blood-red color; if we treat them in their solution with *chlorine*, a yellow body is deposited. They are mostly soluble in water.

*Sulphocyanide of Ammonium*:  $NH_4 + (CyS)^{\wedge}S$ ; is obtained by direct saturation; it is also formed, besides other products, when a solution of sulphocarbonic acid in alcohol is saturated with ammonia; easily soluble deliquescent salt. *Sulphocyanide of potassium*,  $K + (CyS)^{\wedge}S$ . The crystallized salt resembles nitrate of potassa; easily soluble in water; possesses a cooling salty taste; fuses, when the air is excluded, without suffering decomposition, and stiffens to a radiated crystalline mass. *Sesquisulphocyanide of iron*,  $Fe_2 + 3(CyS)^{\wedge}S$ . After evaporation of a solution of hydrate of peroxide of iron in hydrosulphocyanic acid, there remains a red deliquescent mass behind; easily soluble in water and alcohol. *Sulphocyanide of zinc*,  $Zn + (CyS)^{\wedge}S$ , crystallizes in rhombic prisms; easily soluble in water and alcohol. *Sulphocyanide of lead*,  $Pb + (CyS)^{\wedge}S$ , is obtained by double decomposition; it deposits yellow crystals, which increase to great size and possess a strong lustre. Decomposes, in contact with water, into

a basic salt and hydrosulphocyanic acid. *Sulphocyanide of silver*,  $\text{Ag}+(\text{CyS})\text{S}$ , appears as a cheesy precipitate; crystallizes from the ammonia solution in white scales.

*Sulphocyanide of Methyl*:  $\text{Me}+(\text{CyS})\text{S}$ , is obtained, if equal parts of methyloxyd-sulphate of lime and sulphocyanide of potassium, in concentrated solution, are distilled. Colorless, transparent fluid of leek-like odor, of 1.115 sp. gr.; boils at  $132^\circ$ . Is decomposed by *chlorine*, under formation of *para*-chloride of cyanogen and a fluid oil.

Salt-like compounds of sulphocyanogen with organic radicals.  
Sulphocyanide of methyl.

*Sulphocyanide of Ethyl*:  $\text{Ae}+(\text{CyS})\text{S}$ , is in like manner obtained. Completely colorless, thin-flowing fluid, strongly refracting light, of sweet anise-like taste, and penetrating mercaptan-like odor; sp. gr. 1.02; boils at  $146^\circ$ . *Nitric acid* decomposes the compound under the formation of sulphoethyl-sulphuric acid. Bromine forms, with the same, a crystallizable compound. *Sulphocyanide of amyl*,  $\text{Am}+(\text{CyS})\text{S}$ ; oil-like fluid, boils at  $195^\circ$ . Gives, with nitric acid, sulphamyl-sulphuric acid.

Sulphocyanide of ethyl.

Sulphocyanide of amyl.

*Sulphocyanide of Allyl* (Ethereic Mustard Oil),  $\text{All}+(\text{CyS})\text{S}$ , is formed by decomposition of myronic acid, occurring in black mustard seed, under co-operation of myrosin. If the seed be some time digested with water and then distilled, the distillate contains mustard oil. Also, spoonwort and horseradish give mustard oil, by distillation. If the compound of sulphide of mercury-allyl, with chloride of mercury-allyl (*v. Allyl*) be heated with sulphocyanide of potassium, mustard oil goes over at  $130^\circ$ . Pure mustard oil is a colorless fluid of exceeding strong exciting odor, and extremely burning taste; brought upon the skin, it soon draws a blister. Sp. gr. 1.009; boils at  $140^\circ$ ; easily soluble in alcohol and ether. *Nitric acid* attacks mustard oils very actively; in the beginning we obtain a sulphur-yellow, porous, resinous, mass, *nitrosinapyl-resin*,  $\text{N}_3\text{C}_{24}\text{H}_{12}\text{S}_4+3\text{NO}_4$ , which, by farther action, is converted into *nitrosynapyllic acid*, under formation of sulphuric acid. If the mustard oil be treated with great excess of baryta water in the heat, we thus obtain carbonate of baryta and a base *sinapolin*,  $\text{N}_2\text{C}_{14}\text{H}_{12}\text{O}_2$ ; the same decomposition follows, if it be treated with aqueous alkali or with freshly precipitated *oxyhydrate of lead*; in the last case are formed carbonate of lead and sulphide of lead,  $2(\text{C}_8\text{H}_5\text{NS}_2)+6\text{PbO}+2\text{HO}=\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2+4\text{PbS}+2(\text{PbO},\text{CO}_2)$ . If mustard oil be shaken with strong aqueous ammonia, thus vanishes, by degrees, the odor of the oil, and, after a little time, the whole stiffens to a crystalline mass, *thiosinamin*,  $\text{N}_2\text{C}_8\text{H}_8\text{S}_2$ . If mustard oil be brought, by drops, into an alcoholic potassa solution, carbonate of potash is deposited under violent reaction. From the alcoholic solution, water precipitates an oily

Sulphocyanide of allyl.  
(Mustard oil.)

compound which consists of  $N_2C_{14}H_{14}S_2O_2$ , immediately arises still another peculiar compound, containing potassium. *Salts of peroxide of iron*, are not colored red by a watery solution of mustard oil.

*Hydrobisulphocyanic Acid* (Hydrohypersulphocyanic Acid, Hydroxanthanic Acid):  $H + (CyS_2) \cdot S$ . Hydrosulphoferrocyanic acid.

We mix a cold saturated aqueous solution of sulphocyanide of potassium with 6 to 8 fold volume strong hydrochloric acid; the white pap, which is separated, becomes yellow by degrees; after 24 hours this is changed into fine needles, which are washed with water. Crystallizes from the hot aqueous solution in beautiful yellow needles, which are almost insoluble in cold water, slightly soluble in boiling, and somewhat more soluble in alcohol and ether. The acid decomposes at  $240^\circ$ , and, under deposition of sulphur, falls into hydrosulphocyanic acid, sulphocarbonic acid, and compounds poor in sulphur, there remaining, at last, only melamin; according to other accounts, the residue contains hydromellan. *Nitric acid* decomposes the acid into carbonic acid, sulphuric acid, and ammonia. *Chlorine*, in like manner, produces decomposition under formation of chloride of sulphur, of cyanogen, and hydrochloric acid, and a brown-red substance. Brought in contact with *ammonia*, sulphur-milk is separated, and, in the yellow solution, is found neither sulphide of ammonium nor sulphocyanide of ammonium. By the action

Bisulphocyanides of metals.

of *alkalies* upon hydrobisulphocyanic acid, a mixture is formed of sulphocyanides of metals and bisulphocyanides. *Bisulphocyanide of lead*,  $Pb + (CyS_2)S$ , falls as a chrome yellow powder, if acetate of lead be added to a boiling solution of hydrobisulphocyanic acid; *nitrate of silver* is colored yellow, and *bichloride of mercury* yellowish white.

Selenium and cyanogen.

*Selenium* behaves to cyanogen exactly like sulphur.

Compounds of cyanogen with the halogens. Chloride of cyanogen.

*Protochloride of Cyanogen*:  $CyCl$ , is obtained if chlorine gas be brought together with an aqueous solution of hydrocyanic acid, or with moistened cyanide of mercury. Is gaseous at common temperature, of insupportable odor, exciting tears, very caustic, and extremely poisonous. Is solid at  $-18^\circ$ , and appears in long transparent needles; under the pressure of 4 atmospheres it is a colorless clear liquid. Water absorbs 25 volumes, ether 50, and alcohol 100. Fluid chloride of cyanogen, in a tube closed by fusion, changes, after some time, into solid metachloride of cyanogen  $= N_3C_6Cl_3$ .

If chlorine be conducted into a saturated alcoholic solution of hydrocyanic acid in the cold, we thus obtain chloride of ammonium, and a body which forms long, tender, silvery crystals, slightly soluble in water, but easily soluble in alcohol and ether, and consists of



$\text{NC}_8\text{H}_7\text{O}_4\text{Cl}$ , and contains the elements of  $3(\text{C}_4\text{H}_3)\text{O} + 2(\text{CyCl}) + 5\text{HO}$ . If chloride of cyanogen be conducted into a solution of cyanide of mercury in anhydrous alcohol, we obtain an oily fluid which must consist of  $2\text{AeO} + \text{CyCl}$ . If we let *chlorine*, in excess, act upon hydrocyanic acid, in aqueous solution, we thus obtain hydrochloric acid and a fluid compound which boils at  $20^\circ$ , powerfully excites tears, and consists of  $\text{N}_3\text{C}_6\text{Cl}_2\text{H} = 2(\text{CyCl}) + \text{H Cy}$ . Chloride of cyanogen forms, with *ammonia gas*, a white crystalline *body*  $= 2\text{NH}_3 + \text{CyCl}$ , which is not decomposed by hydrochloric acid.

*Metachloride of Cyanogen* (solid Chloride of Cyanogen):  $\text{N}_3\text{C}_6\text{Cl}_3 = \text{Cy}_3\text{Cl}_3$ , arises by transposition of the preceding compound. Is obtained, when anhydrous hydrocyanic acid is decomposed by dry chlorine in the sunlight. Crystallizes in white needles; of slight taste, and mouse-like odor; sp. gr. 1.32; melts at  $140^\circ$ ; sublimes at  $190^\circ$ ; slightly soluble in cold water, easily soluble in alcohol and ether. Boiled with water we obtain hydrochloric and cyanurenic acid. Brought together with *ammonia gas*, a white powder is formed  $= 3\text{NH}_3 + \text{Cy}_3\text{Cl}_3$ .

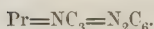
*Bichloride of Cyanogen*:  $\text{CyCl}_2$ , must be obtained if a concentrated solution of cyanide of mercury be exposed to the sunlight in a bottle filled with chlorine gas. We obtain a heavy oil-like fluid. If the alcoholic solution be mixed with water, a solid body is deposited. If into a bottle filled with chlorine gas we bring a boiling solution of cyanide of mercury, there separates in the sunlight a heavy oily liquid of extremely strong odor, exciting tears, and a caustic taste; it consists of  $\text{N}_2\text{C}_6\text{Cl}_7 = 2(\text{CyCl}_2) + \text{C}_2\text{Cl}_3$ . If nitric acid oxidizes the compound, we obtain a yet caustic product  $= \text{N}_2\text{C}_4\text{Cl}_4\text{O}_2 = \text{CyCl}_3 + \text{Cy} \begin{Bmatrix} \text{O}_2 \\ \text{Cl} \end{Bmatrix}$ .

*Protobromide of Cyanogen*:  $\text{CyBr}$  is obtained like protochloride of cyanogen; crystallizes in white, slender, long prismatic needles; possesses a penetrating disagreeable odor; extremely poisonous, and very volatile. Gives, with *ammonia*, a fluid compound  $= 6\text{NH}_3 + \text{CyBr}$ , which, in the air, becomes solid under evolution of ammonia. This solid *body* is  $2\text{NH}_3 + \text{CyBr}$ .

*Protiodide of Cyanogen*:  $\text{CyI}$ , is obtained by heating cyanide of mercury with iodine and some water in a flask with a long neck. In the neck of the flask the iodide of cyanogen condenses in slender, woolly needles; possesses a highly penetrating odor, strongly exciting the eyes, and a biting taste. Easily soluble in water, alcohol, and ether. If the aqueous solution be shaken with mercury, thus we obtain iodide of mercury and cyanogen. Gives, with *ammonia*, a fluid compound  $= 3\text{NH}_3 + \text{CyI}$ , which becomes solid at  $50^\circ$  under formation of  $\text{NH}_3, \text{CyI}$ .

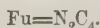


## PARABAN:



*Parabanic Acid:*  $\text{HO}, \text{PrO}_2 = 2\text{HO}, \text{PrO}_4$ , is obtained, if 1 part uric acid is dissolved in 8 parts moderately concentrated nitric acid and the solution evaporated to syrup-thickness (*v. Uric Acid*). Crystallizes in hexagonal, very sour-tasting prisms; easily soluble in water; is not decomposed in the aqueous solution, even by the presence of acid itself; on the contrary, the parabanates are converted into oxalic acid by the slightest warming under absorption of 2 atoms water.

## FULMINAN:



By fulminan is understood a hypothetical radical polymeric with cyanogen, of which it is assumed that it forms with *oxide of zinc, of copper, of mercury, and of silver*, or with their metals, paired radicals, which, with 2 or 3 atoms oxygen, produce acids which with bases give violently exploding salts, named fulminates. According to one view are given, different fulminic acids corresponding to the formulæ

Zinc-fulminic acid,	. . . .	$\text{HO} + (\text{ZnO})\text{FuO}_2.$
Copper-fulminic “	. . . .	$\text{HO} + (\text{CuO})\text{FuO}_2.$
Mercury-fulminic acid,	. . . .	$\text{HO} + (\text{Hg}_2\text{O})\text{FuO}_2.$
Silver-fulminic “	. . . .	$\text{HO} + (\text{AgO})\text{FuO}_2.$

*Fulminate of silver* consists, then, of  $\text{Ag} + \text{O}(\text{AgO})\text{FuO}_2$ . If hydrochloric acid be added to this compound, only half of the silver is precipitated as chloride of silver, under formation of  $\text{HO} + (\text{AgO})\text{FuO}_2$ ; hence it follows that fulminate of silver cannot be denoted by  $2\text{AgO} + \text{N}_2\text{C}_4\text{O}_2$ , for, according to this formula, both atoms of silver would be precipitated. According to the other view, it is assumed that the metal is an essential constituent of a radical  $=(\text{MN}_2\text{C}_4)$ , which, with 3 atoms of oxygen, forms fulminic acid, and this view is below assumed. According to a third opinion, the fulminic acids are paired combinations of nitrogen-metal with  $\text{NC}_4\text{O}_3$ ; the silver-fulminic acid then consists of  $\text{HO} + (\text{AgN})\text{NC}_4\text{O}_3$ . The mercury-fulminate of protoxide of mercury (fulminating mercury) and the silver-fulminate of silver (fulminating silver) are obtained, if the nitric acid solution of the nitrate of either metal be brought together with alcohol, under evolution of nitrogen gas, or if  $\text{NO}_4$  be conducted into the alcoholic solution of the salts named. If silver-fulminate of silver,  $\text{AgO} + (\text{AgN}_2\text{C}_4)\text{O}_3$ , be digested with metallic zinc or copper, thus we obtain zinc-fulminate or copper-fulminate under precipitation

of silver. The metal-fulminic acids, as well as their salts, all possess the capability of violently exploding, hence their production and treatment must take place with the greatest caution.

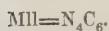
*Zinc-fulminic Acid*:  $\text{HO}(\text{ZnN}_2\text{C}_4)\text{O}_3$ , is obtained, if the solution of the baryta salt be accurately decomposed, by sulphuric acid. Known only in aqueous solution, it reacts acid, and possesses an odor like hydrocyanic acid. The salts are best obtained if the baryta salt be precipitated by a sulphate. The *potassa salt* crystallizes in small colorless rhombic prisms, reacts alkaline, easily soluble in water. The *baryta salt* crystallizes in small shining prisms; it is obtained by decomposing the zinc salt with baryta; easily soluble in water. The *zinc salt*,  $\text{ZnO} + (\text{ZnN}_2\text{C}_4)\text{O}_3$ . We digest metallic zinc a long time with mercury-fulminate of protoxide of mercury, and evaporate the obtained solution in a vacuum. Crystallizes in thin, white, rhombic scales, which no longer dissolve in water. Explodes violently at  $176^\circ$ .

*Copper-fulminic Acid*:  $\text{HO} + (\text{CuN}_2\text{C}_4)\text{O}_3$ . Only known in combination with protoxide of copper =  $\text{CuO} + (\text{CuN}_2\text{C}_4)\text{O}_3$ . The copper salt is obtained by shaking copper filings with mercury-fulminate of protoxide of mercury. Crystallizes in light green hexagonal pyramids; explodes with extreme violence, and a large white flame. The *ammonia salt* is decomposed by hydrosulphuric acid into urea and sulphocyanide of ammonium.

*Mercury-fulminate of Protoxide of Mercury* (Fulminating Mercury):  $\text{Hg}_2\text{O} + (\text{Hg}_2\text{N}_2\text{C}_4)\text{O}_3$ . Half an ounce of mercury is dissolved in 6 ounces nitric acid of 1.3 sp. gr., in a vessel placed in hot water, and to the solution cooled to  $12^\circ$  4 oz. alcohol of 0.833 sp. gr. are added. The mixture is held in boiling water until a white vapor is evolved. After a few minutes the fulminating mercury separates as a very violently explosive crystalline powder.

*Silver-fulminic Acid*:  $\text{HO} + (\text{AgN}_2\text{C}_4)\text{O}_3$ , is precipitated as a white powder, if the potassa salt be mixed with nitric acid; insoluble in cold water, easily soluble in hot; crystallizes from the boiling solution in needles, which explode with extreme violence. The *potassa salt* crystallizes in white shining leaflets, tastes metallic, dissolves in 8 parts boiling water; chlorides of metals produce, in the solution, no precipitate. The *silver salt* (fulminating silver),  $\text{AgO} + (\text{AgN}_2\text{C}_4)\text{O}_3$ , is obtained like fulminating mercury. Explodes the most violently of all fulminates, by pressure, by the electric spark, and by contact with concentrated sulphuric acid. Hydrochloric acid decomposes the salt; in the beginning silver-fulminic acid becomes free, but it soon, by further action of hydrochloric acid, is decomposed into chloride of silver, hydrocyanic acid, and another acid which is said to consist of  $\text{NC}_2\text{Cl}_5 + \text{H}$ .

## MELLAN:



*Mellan* (Mellon) is a radical which, in its chemical relations, agrees with cyanogen in many respects. It is formed when dry chlorine gas is conducted over heated sulphocyanide of potassium, farther by heating hydrobisulphocyanic acid, as well as the compounds of ammonia with chloride, bromide, and iodide of cyanogen. Pure *mellan-potassium* is obtained, if the residue which remains after heating the sulphocyanide of ammonium (melam) be melted with an equal weight of dry sulphocyanide of potassium, until no more evolution of ammonia, sulphocarbonic and hydrosulphuric acid is observed, and, after cooling, if the aqueous solution of the fused mass be mixed with alcohol. *Mellan-potassium* separates in fine crystals; these are washed with alcohol, then dissolved in water, the solution boiled with charcoal, and from the colorless fluid the *mellan-potassium* is precipitated by alcohol. Pure *mellan* is obtained by heating *mellan-mercury* in a retort. It is of a pale lemon color, is tasteless and inodorous, insoluble in water, alcohol, ether, and dilute acids. Decomposes in white heat into cyanogen gas and nitrogen gas. If we boil *mellan* with nitric acid, we obtain nitrate of ammonia and *cyanylic acid*, which has the same constitution as cyanurenic acid. In *concentrated sulphuric acid*, it is soluble without decomposition. By warming with chlorine, it gives a white volatile body, which irritates the eyes. If *mellan* be fused with *hydrate of potassa*, we obtain cyanurenate of potassa under evolution of ammonia.

Compounds of  
mellan with hy-  
drogen.

*Hydromellanic Acid*:  $\text{HMII}$ . If concentrated acetic acid be added to a hot solution of *mellan-potassium*, the obtained mass evaporated to dryness, and from the residue the acetate of potassa extracted by alcohol, there remains a yellowish-white, earthy, tasteless, and inodorous body, which is soluble in water, reddens litmus-paper, and consists of 1 atom *mellan-potassium* and 2 atoms *hydromellanic acid*. This body expels several organic acids from their compounds, and decomposes iodide of potassium. By heating 17 per cent. cyanide of potassium remains.

With metals.

*Mellan* combines with *potassium* under appearance of fire. The insoluble metal compounds are obtained by double decomposition. By glowing, the cyanides of metals evolve cyanogen gas and nitrogen gas; the alkali-*mellan* metals leave behind cyanides of the metals; the heavy metal compounds leave carburets of the metals.

*Mellan-potassium*,  $\text{KMII} + 5\text{aq}$ , crystallizes from the hot saturated solution in fine, colorless needles, which effloresce in the air. *Mellan-lead*,  $\text{PbMII} + 5\text{aq}$ , is obtained as a white precipitate by

double decomposition. *Mellan-silver*,  $\text{AgMll}$ , appears as a jelly-like precipitate, which, dried at  $120^\circ$ , contains no water.

*Sulpho-mellan*:  $\text{MllS}$ , is not known isolated. If we dissolve the so-called sulphide of cyanogen (which is precipitated, when chlorine is conducted into a solution of sulphocyanide of potassium, and consists of  $\text{N}_2\text{C}_4\text{H}_2\text{S}_4\text{O}$ ) in a hot concentrated solution of  $\text{KS, HS}$ , and boil the solution 12 hours, thus is formed, upon the addition of acetic acid, a precipitate, which consists of sulphur and *hydrosulpho-mellanic acid*. Ammonia absorbs the acid of the precipitate in the cold; if the solution be bleached by boiling with animal charcoal, we obtain, by the addition of an acid, the hydrosulphomellanic acid, as a snow-white body. Hydrosulpho-mellanic acid consists of  $\text{N}_4\text{C}_6\text{H}_4\text{S}_4$ . It separates from the boiling aqueous solution in white acicular crystals; is tasteless; reddens litmus; and is soluble in water, alcohol, and ether. If we heat it to  $150^\circ$ , it decomposes into mellan and hydrosulphuric acid. Only 1 atom of hydrogen can be replaced by 1 atom of metal; it appears therefore as a paired acid, which contains 3 atoms of  $\text{HS}$  as pairing, and its probable formula is  $\text{H} + (3\text{HS})\text{MllS}$ . The *sulpho-mellan metals*  $= \text{M} + (3\text{HS})\text{MllS}$ , can be directly obtained; the combinations with the alkali metals are soluble in alcohol and ether, and crystallizable; also with the heavy metals sulpho-mellan,  $(3\text{HS})\text{MllS}$ , forms crystallizable compounds; the alkali metal compounds evolve by heating sulphide of ammonium and hydrocyanic acid.

Mellan and sulphur.

Hydrosulpho-mellanic acid.

Sulpho-mellan metals.



## FOURTH DIVISION.

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### HYDROAZOCARBYLS.

In this chapter a series of organic compounds is treated, closely allied to the azocarbyls, by whose transposition they, in part, are formed. All compounds of this class have, in common with those of cyanogen, great transposition-power, and from many of their relations it would appear that they contain cyanogen or another azocarbyl, or they go over into these easily. On account of the mutability of these compounds, it is very difficult to fix upon their rational formulæ, since, with regard to their products of decomposition, several may be made with equal correctness. Most of the compounds, which are nearly all acids, appear to contain one common substance—*uren* as a pairling.

UREN :



By *uren*, a ternary radical is understood, which is formed by the transposition of cyanogen; it is metameric with anhydrous hydrocyanic acid and can unite in different proportions with oxygen and sulphur; these combinations have great tendency to appear as pairlings. With the *uren* combinations may be classed:—

Oxide of Uren, . . . . .	UrO <sub>2</sub> ,
Hydrosulphbiurenic acid, . . .	H + (2UrS)~S,
Hydrosulphurenic acid, . . .	H + (UrS)~S,
Hydrobisulphurenic acid, . . .	H + (UrS <sub>2</sub> )~S,
Hydrotrisulphurenic acid, . . .	H + (UrS <sub>3</sub> )~S,
Cyanurenic acid, . . . . .	2HO + (UrO <sub>2</sub> )~2CyO.
Et cetera.	

Compounds of uren.	<i>Oxide of Uren</i> (Insoluble Cyanuric Acid): Ur
Oxide of <i>uren</i> .	O <sub>2</sub> . If the hydrate of cyanic acid be exposed to a temperature of about 0°, it is changed into a white inodorous, porcelain-like mass; insoluble in water, alcohol, ether, and acids, consisting of oxide of <i>uren</i> , HO,NC <sub>2</sub> O=(NC <sub>2</sub> H)O <sub>2</sub> .

If oxide of uren be subjected to dry distillation, it is again converted into hydrate of cyanic acid. Heated with *concentrated sulphuric acid*, it separates into carbonic acid and ammonia. If the solution of oxide of uren in caustic alkalies be evaporated, there remain cyanurenic acid salts. With ammonia, oxide of uren forms a paired base—*Urea*.

*Hydrosulphbiurenic Acid* (Hydroflaveanic Acid):  $H + (2UrS)^{\wedge}S$ . This compound is obtained, when 2 measures of cyanogen gas and 3 measures of hydrosulphuric acid gas, in moist state, come in contact with each other over mercury. Yellow transparent crystals; easily soluble in water and alcohol; the solution has no acid reaction; very mutable; soluble without decomposition in potassa-lye, but by boiling we obtain sulphocyanide of potassium, cyanide of potassium, and sulphide of potassium; by being boiled with dilute lye, we obtain ammonia, oxalic acid, and sulphide of potassium.

Hydrosulph-  
biurenic acid.

*Hydrosulphurenic Acid* (Hydrorubeanic Acid):  $H + (UrS)^{\wedge}S$ . If we conduct cyanogen gas and hydrosulphuric acid together into alcohol, with the precaution that hydrosulphuric acid is always present in excess, small red crystals are separated, which, by repeated crystallization from the hot alcoholic solution, become purified. Beautiful orange-red crystals are produced. By cautious heating it is sublimable; but little soluble in water and alcohol. Chlorine gas and hydrochloric acid gas, when cold, do not act upon this compound; by boiling with dilute hydrochloric acid, we obtain oxalic acid, ammonia, and hydrosulphuric acid. If to a cold alcoholic solution we add acetate of lead, thus is produced a lively yellow precipitate  $= Pb + (UrS)S$ . If the lead compound be boiled with water, cyanogen gas escapes,  $PbS$  is formed, and the solution contains hydrosulphurenic acid and hydrosulphbiurenic acid. *Sulphuren*,  $NC_2HS_2$ , is metameric with hydrosulpho-cyanic acid.

Hydrosulph-  
urenic acid.

*Hydrobisulphurenic Acid*:  $H + (UrS_2)^{\wedge}S$ . Ammoniumbisulphuren,  $NH_4 + (UrS_2)S$ , is obtained when 1 volume anhydrous alcohol, saturated with ammonia gas, is left to stand one or two hours in a closed vessel with 0.16 volumes sulpho-carbonic acid, and the clear fluid, quickly withdrawn from the separated sulpho-carbonate of sulphide of ammonium, is by degrees exposed to a temperature of  $0^{\circ}$ . We obtain crystals of the ammonium compound. If the salt be dissolved in 3 parts water, and to the solution hydrochloric acid be quickly added, the acid is separated as an oily, colorless fluid, which is very quickly decomposed. The ammonium compound forms with the metal-salts precipitates of bisulphuren-metals.

Hydrobisulph-  
urenic acid.

*Hydrotrisulphurenic Acid*:  $H + (UrS_3)^{\wedge}S$ . This acid is precipitated in shining crystalline flakes, if chlorine gas be conducted into the solution of am-

Hydrotrisulph-  
urenic acid.

monium-bisulphuren. Colorless and odorless, but slightly soluble in water, more easily so in alcohol, ether, and acetone. If the freshly precipitated acid be warmed with perchloride of iron, it is colored deep blood-red. By being warmed with potassa-lye, it is separated into sulphide of potassium and sulphocyanide of potassium.

Compounds obtained by the action of nitric acid and chlorine upon sulphohydrocyanic acid.

*So-called Sulphide of Cyanogen.* If we conduct chlorine into a cold solution of sulphocyanide of potassium, there is separated a yellow body, which consists of  $N_4C_8H_4S_8O$ , or, according to other statements, of  $N_2C_4H_2S_4O$ , and may be considered as a combination of trisulphuren with oxysulphuren  $= 2(UrS_3) +$

$Ur \left\{ \begin{array}{l} O \\ S \end{array} \right.$ . If we digest for three hours 3 parts of this substance, which has been called sulphide of cyanogen, with 4 parts potassa and 25 parts water, and boil the mass half an hour, a black substance is separated, and if to the abfiltered fluid we add dilute hydrochloric acid, a yellow precipitate is formed. If we dissolve this precipitate in hot alcohol, we obtain from the filtered solution by evaporation *hydrothiocyanic acid*, which is said to consist of  $N_5C_{10}H_6S_{12}O_2$ . A lemon-colored crystalline powder of very sharp and bitter taste; dissolves in 1000 parts cold and 2.5 parts boiling water. This acid must be a tetra-basic hydrogen acid, which contains 2 more atoms of water of crystallization. With the bases it forms thiocyanides of metals and water. By boiling, it expels carbonic acid from the alkali salts.

If we add *chlorine* to the *boiling solution of sulphocyanide of potassium*, a yellow substance is precipitated, said to consist of  $N_4C_8H_3S_9O$ , whose alcoholic solution forms yellow precipitates with salts of lead and silver. If we boil the aqueous solution of sulphocyanide of potassium with nitric acid, a yellow substance is precipitated, which has probably the same constitution.

*Cyanurenic Acid* (Cyanuric Acid, Pyrouric Acid):  
Cyanurenic acid.  $2HO + (UrO_2) \cdot 2CyO = 2HO + N_3C_6HO_4 = 2H + OCu$

$O_4$ . This acid is formed by the dry distillation of uric acid and of urea, in the decomposition of metachlorcyanogen by water, in the decomposition of cyanate of potassa by acetic acid, etc. If we expose hydrochlorate of urea to a temperature of  $140^\circ$ , we obtain chloride of ammonium and pure cyanurenic acid. Crystallizes from the aqueous solution in oblique rhombic prisms containing 4 atoms water of crystallization, which they lose by gently heating. From the hot concentrated sulphuric acid solution the acid is slowly separated; thus we obtain it anhydrous, in four-sided columns; colorless, odorless, almost tasteless; reddens litmus. Separates by distillation into hydrate of cyanic acid. *Cyanurate of potassa*,  $2KO + CuO_4$ , is obtained when acetic acid in small quantities is added to a concentrated solution

of cyanate of potassa. The potassa salt, which is separated, is dissolved in potassa, and the solution mixed with alcohol, by which the salt is precipitated in white needles. In contact with water, it separates into free potassa and acid cyanurate of potassa  $= 2\text{K}\text{O}, 2\text{H}\text{O}, 2\text{C}\text{ur}\text{O}_4$ , which crystallizes in white shining cubes; not easily soluble in water.

*Cyanurate of Baryta*:  $2\text{Ba}\text{O} + \text{C}\text{ur}\text{O}_4 + 3\text{aq}$ , is precipitated, when to a hot solution of the acid, an excess of baryta water is added. The *acid baryta salt*,  $2\text{Ba}\text{O}, 2\text{H}\text{O}, 2\text{C}\text{ur}\text{O}_4$ , we obtain as a crystalline powder, when baryta water is dropped into a boiling solution of cyanurenic acid so long as the precipitate is redissolved.

*Cyanurate of Silver*,  $2\text{Ag}\text{O} + \text{C}\text{ur}\text{O}_4$ , is obtained when acetate of silver is added to a hot solution of cyanurenic acid. A colorless crystalline powder; insoluble in water and acetic acid, and combines with 2 atoms of ammonia. If we mix a hot solution of the acid with an excess of ammonia, and then with nitrate of silver, we obtain a crystalline powder, which contains ammonia, but, dried at  $300^\circ$ , consists of  $3\text{Ag}\text{O} + \text{C}\text{ur}\text{O}_4$ .

*Cyanurate of Methyl* is produced in small, colorless crystals, which melt at  $140^\circ$ , and evaporate at  $295^\circ$ .

*Cyanurate of Ethyl* crystallizes from the alcoholic solution; fuses at  $85^\circ$ ; boils at  $276^\circ$ . Both of these compounds are obtained when methyloxyd-sulphate or ether-sulphate of potassa is distilled with cyanurate of potassa; the formula for these compounds is said to be  $3\text{Me}\text{O}$  or  $3\text{Ac}\text{O}, \text{N}_3\text{C}_6\text{O}_3$ .

*Mellanurenic Acid*:  $\text{N}_4\text{C}_6\text{H}_4\text{O}_4$ . If perfectly dry urea be subjected to a slow distillation, most of the urea is not converted into cyanurenic acid but into mellanurenic acid; the latter remains, when the residue is boiled out with water. A brilliant white chalk-like powder; insoluble in water, easily soluble in acids and alkalies; by being long treated with alkalies, it separates into ammonia and cyanic acid. Mellanurenic acid may be considered as a paired compound of urea with cyanic acid  $= (\text{N}_2\text{C}_2\text{H}_4\text{O}_2), 2\text{C}\text{y}\text{O}$ .

*Allophanic Acid*:  $\text{HO} + \text{N}_2\text{C}_4\text{H}_3\text{O}_5$ , is formed when the vapor of hydrate of cyanic acid is conducted into anhydrous alcohol. We obtain allophanate of ethyl; the acid is not known isolated, for it separates at once into carbonic acid and urea. If we treat the oxide-of-ethyl compound with the pure bases, we obtain allophanic acid salts; but they also separate, when heated, into carbonic acid salts and urea. The *potassa salt* crystallizes in leaflets, like chlorate of potassa. The *baryta salt* forms connected needles; if it be heated in a retort, carbonate of ammonia escapes, and the residue contains cyanate of baryta.

*Allophanate of Ethyl* appears as a white crystalline powder,



which out of the alcoholic-etheric solution appears, by slow evaporation, in clear, tasteless, and odorless crystals of mother-of-pearl lustre. By dry distillation, it separates into alcohol and cyanurenic acid. If we conduct the vapor of cyanic acid into *wood-spirit* or *amyl-spirit*, we obtain the corresponding compound of oxide of methyl or of amyl.

*Allophanic Acid* probably consists of urea—1 atom H plus oxalic acid  $=(\text{N}_2\text{C}_2\text{H}_3\text{O}_2), \text{C}_2\text{O}_3 = (\text{NC}_2\text{H}, \text{O}_2) \text{NH}_2, \text{C}_2\text{O}_3$  or urenydamid-oxalic acid.

*Trigenic Acid*:  $\text{HO}, \text{N}_3\text{C}_8\text{H}_5\text{O}_3 = \text{HO} + (\text{Ur}_3) \text{C}_2\text{H}, \text{O}_3$ , is obtained when the vapor of hydrate of cyanic acid is conducted into aldehyd, and the action is lessened by cooling. A ropy mass remains, consisting of trigenic acid, oxide of uren, and aldehyd-ammonia. The mass is boiled with moderately concentrated hydrochloric acid, and filtered; after cooling, trigenic acid separates in small stelliform grouped prisms; tastes feebly acid; not easily soluble in water, insoluble in alcohol. By heating, it separates into *chinolin* and cyanic acid.

*Uric Acid* (Lithic Acid):  $= 2\text{HO}, (\text{NC}_2\text{H}, \text{NH}) \text{N}_2$  Uric acid.  $\text{C}_8\text{O}_4$ . Uric acid occurs only in the animal body. It is found in the urine of carnivorous animals, in the urinary sediments in many diseases, it frequently causes the formation of urinary calculi. Uric acid is found most abundant in the excrements of birds, snakes, lizards, snails, and insects, and almost always in combination with ammonia (*guano*). The excrements of large serpents are best adapted for its production; we leave them lying exposed to the air, until they become nearly white, and then they consist mainly of urate of ammonia. If we dissolve this latter substance in warm concentrated sulphuric acid, and mix the clear, generally brownish-yellow solution with small portions of water (under constant stirring) as long as a precipitate is produced, we obtain the uric acid as a dazzling white powder. We can also produce from the excrements pure urate of potassa, which is decomposed by hydrochloric acid. White, tasteless, inodorous crystal scales, soluble in 15,000 parts cold and 1800 parts boiling water; reddens litmus. If hydrochloric acid be added to a cold solution of urate of potassa, we obtain crystals, in the form of scales, which contain 1 atom water of crystallization.

*Decomposition of Uric Acid*. Uric acid may be considered as a paired compound of urenimid with  $\text{N}_2\text{C}_8\text{O}_4 = (\text{NC}_2\text{H}, \text{NH})$ , with  $\text{N}_2\text{C}_8\text{O}_4$ ; further,  $\text{N}_2\text{C}_8\text{O}_4$  contains the elements of 2 atoms cyanogen and 2 atoms of oxatylous acid  $2\text{C}_2\text{O}_2$ . If urenimid absorbs the elements of 2 atoms water, we obtain urea,  $\text{NC}_2\text{HO}_2, \text{NH}_3$ , and if the elements of 4 atoms water with 2 atoms oxygen are united to  $\text{N}_2\text{C}_8\text{O}_4$ , thus alloxan is formed  $= \text{N}_2\text{C}_8\text{H}_8\text{O}_{10}$ . The hypothetical compound  $\text{N}_2\text{C}_8\text{O}_4$  has been called urilic acid. This supposition explains satisfactorily the phenomena of decomposition exhibited

by uric acid. By dry distillation, uric acid separates into carbonate of ammonia, hydrocyanic acid, urea, and cyanurenic acid.

If, to a mixture of uric acid and water, heated nearly to boiling, *superoxide of lead* be added as long as its color disappears, we thus obtain *allantoin*,  $\text{HO}, \text{N}_4\text{C}_8\text{H}_5\text{O}_5$ , *urea* and oxalic acid, with the evolution of carbonic acid and 4 atoms of uric acid  $\text{N}_8\text{C}_{20}\text{H}_4\text{O}_8 + 10\text{HO} + \text{O}_4 = \text{HO}, \text{N}_4\text{C}_8\text{H}_5\text{O}_5 + 2(\text{N}_2\text{C}_2\text{H}_4\text{O}_2) + 4\text{C}_2\text{O}_3$ . If to *nitric acid* of 1.41 to 1.45 sp. gr. there be gradually added half its weight of uric acid (and by this means each heating be avoided), whilst equal quantities of nitrogen gas and carbonic acid gas escape, and the whole stiffens to a thick paste of alloxan, simultaneously nitrate of ammonia is formed. According to the formula  $(\text{NC}_2\text{H}, \text{NH})^-, \text{N}_2\text{C}_8\text{O}_4$ , by taking 4 atoms water and 2 atoms oxygen  $\text{N}_2\text{C}_8\text{O}_4$  is changed into alloxan; simultaneously urenimid, by decomposition of water, separates into ammonia (which is united with nitric acid) and into oxide of uren,  $\text{NC}_2\text{HO}_2$ , which is oxidized by the produced nitrous acid, forming carbonic acid and water, whilst nitrogen escapes,  $\text{NC}_2\text{HO}_2 + \text{NO}_3 = 2\text{N} + 2\text{CO}_2 + \text{HO}$ . If dilute instead of concentrated nitric acid be used, instead of alloxan, we obtain *alloxantin*,  $\text{N}_2\text{C}_8\text{H}_5\text{O}_{10}$ ; now is  $\text{N}_2\text{C}_8\text{O}_4 + 5\text{HO} + \text{O} = \text{N}_2\text{C}_8\text{H}_5\text{O}_{10}$ . If the solution of uric acid in *moderately concentrated nitric acid*, be evaporated to a certain degree after the evolution of gas has ceased, the alloxan disappears, and at a certain point of concentration we obtain crystals of *parabanic acid*; 1 atom alloxan separates with 2 atoms oxygen into 2 atoms hydrate of parabanic acid, 2 atoms carbonic acid, and 2 atoms water,  $\text{N}_2\text{C}_8\text{H}_4\text{O}_{10} + \text{O}_3 = 2(\text{HO}, \text{NC}_3\text{O}_2) + 2\text{CO}_2 + 2\text{CO}$ . If the solution of parabanic acid be over-saturated with ammonia, it is converted, under absorption of water into *oxaluric acid*  $\text{N}_2\text{C}_6\text{H}_4\text{O}_8$ ;  $\text{N}_2\text{C}_8\text{O}_4 + 4\text{HO} = \text{N}_2\text{C}_6\text{H}_4\text{O}_8$ . If, on the other hand, the solution of parabanic acid in the acid fluid be farther evaporated without being previously saturated with ammonia, we obtain, under constant evolution of carbonic acid, crystals of nitrate of urea,  $\text{N}_2\text{C}_6\text{O}_4 + 4\text{HO} + \text{O}_2 = \text{N}_2\text{C}_2\text{H}_4\text{O}_2 + 4\text{CO}_2$ . If a solution of uric acid in *very dilute nitric acid*, which contains *alloxantin*, be evaporated so far that the latter will be separated in cooling, and if then we saturate it with ammonia, the fluid is colored purple-red, and there are gradually deposited shining green crystals of *murexyd* (testing uric acid).

If we treat uric acid with *chlorate of potassa* and *hydrochloric acid*, it completely separates into alloxan and urea. If we heat *dry uric acid* in *chlorine gas*, it almost all disappears, whilst hydrochloric and cyanic acid are formed. If into a boiling solution of uric acid chlorine gas be conducted, quadroxalate of ammonia is obtained.

*Urates.* Uric acid is a very weak acid; it forms neutral and acid salts, which either correspond to the formulæ  $\text{RO}, \text{N}_2\text{C}_5\text{HO}_2$

and  $\text{RO}, \text{HO} + 2(\text{N}_2\text{C}_5\text{HO}_2)$ , or  $2\text{RO} + \text{N}_4\text{C}_{10}\text{H}_2\text{O}_4$  and  $\text{RO}, \text{HO} + \text{N}_4\text{C}_{10}\text{H}_2\text{O}_4$ . The acid salts are not easily soluble in water, and appear as earthy, tasteless powders. *Urate of potassa*,  $\text{KO}, \text{LiO}$ . We boil a solution of uric acid in dilute potassa-lye, excluding the air, until fine needles are formed, and wash the salt with alcohol. A white, crystalline powder, reacting strongly alkaline; exposed to the air it changes into the acid salt by forming carbonate of potassa; dissolves in 36 parts water of  $15^\circ$ . The *acid salt*,  $\text{KO}, \text{HO}, 2\text{LiO}_2$ , is separated as a granular powder; not easily soluble; if into the potassa solution of uric acid carbonic acid be conducted, the salt dries, forming a hard mass. *Urate of soda*,  $\text{NaO}, \text{LiO}_2 + \text{aq}$ ; crystallizes from the boiling solution in hard masses, which react alkaline and dissolve in 62 parts water at  $15^\circ$ . The *acid soda salt*,  $\text{NaO}, \text{HO}, 2\text{LiO}_2$ , appears, after being dried, as a white, light powder; dissolves in 1150 parts cold and in 124 parts boiling water. *Urate of baryta*,  $\text{BaO}, \text{LiO}_2$ ; a heavy, granular, alkaline, reacting salt. The *acid baryta salt*,  $\text{BaO}, \text{HO}, 2\text{LiO}_2 + \text{aq}$ , is a white powder; insoluble in water, alcohol, and ether. Uric acid is dissolved in a solution of borax, also in ordinary phosphate of soda as urate of soda.

*Allantoin*:  $\text{HO}, \text{N}_4\text{C}_8\text{H}_5\text{O}_5$ , is found in the allantoid fluid of the cow and in the liquor amnii; if the former be evaporated to one-fourth, it is separated in crystals. Allantoin is formed by the decomposition of uric acid by means of superoxide of lead. From the hot aqueous solution water-clear, shining, quadrilateral crystals form; tasteless; inodorous; soluble in 400 parts cold water and in 30 parts boiling; by distillation, it separates into carbon, carbonate and cyanate of ammonia. When exposed to heat, caustic alkalies decompose it into ammonia and oxalic acid. If we treat uric acid in alkali solution with *ferricyanide of potassium*, it is at first converted into allantoin, and this, by further decomposition, into *lantanuric acid*, which is a gummy, acid-reacting mass; easily soluble in water. Lantanuric acid consists of  $\text{HO}, \text{N}_2\text{C}_6\text{HO}_5$ . If nitrate of silver be added to a solution of allantoin, a white precipitate is produced consisting of  $\text{AgO}, \text{N}_4\text{C}_8\text{H}_5\text{O}_5$ .

*Alloxan* (Erythric Acid):  $\text{N}_2\text{C}_8\text{H}_4\text{O}_{10} = 2\text{HO}, \text{N}_2\text{C}_8\text{H}_2\text{O}_9$  (?), arises by the decomposition of uric acid by nitric acid of 1.42 sp. gr., or by the action of hydrochloric acid and chlorate of potassa upon uric acid. It is best obtained, when 4 ounces of uric acid and 8 ounces moderately concentrated nitric acid are mixed together, and into the mixture 1 ounce of pulverized chlorate of potassa is gradually brought. We dilute with water, and conduct into the clear solution hydrosulphuric acid, whereby alloxan is precipitated as alloxantin, whilst the nitrate of urea remains dissolved. The precipitated alloxantin is mixed with



double its volume of boiling water, and nitric acid added in drops so long as binoxide of nitrogen escapes. After cooling, alloxan is separated in crystals. In ordinary temperature large rhombic octohedrons are formed, which contain 6 atoms water of crystallization, and effloresce, when exposed to the air. The crystals, obtained from the hot solution, are anhydrous; easily soluble in water; colors the skin red; tastes unpleasantly metallic, briny, and acid; reddens litmus, but does not unite with bases. If the solution be boiled a short time, 3 atoms of alloxan separate into 2 atoms allantoin, 2 atoms of hydrate of parabanic acid, and 2 atoms carbonic acid; treated with *superoxide of lead* carbonic acid and urea are obtained.

*Alloxantin*:  $\text{N}_2\text{C}_8\text{H}_5\text{O}_{10} = 2\text{HO}, \text{N}_2\text{C}_8\text{H}_3\text{O}_8$ , is formed, Alloxantin.  
 1st. By the action of dilute nitric acid upon uric acid; 2d. When hydrosulphuric acid is conducted into a cold solution of alloxan, under separation of sulphur; also by the action of zinc and hydrochloric acid upon alloxan. Alloxantin crystallizes from the boiling aqueous solution in oblique, quadrilateral, colorless prisms, which contain 3 atoms of water; reddens litmus; not easily soluble in cold water, more easily in boiling. If to the cold solution baryta water be added, a violet-blue precipitate is formed, which, by being warmed again disappears. If a solution of alloxantin in water freed from air, be boiled a long time, it colors the liquid a reddish purple. But the color soon disappears, and in cooling uramil is separated, and from the yellow solution we obtain crystals of murexyd; at last, the solution stiffens to a gelatinous mass. Alloxantin and *ammonia* give uramil and alloxan. Dilute *nitric acid* converts alloxantin into alloxan in the same manner as selenious acid. If a *boiling solution of alloxantin* be mixed with *ammonia*, and boiled until the red color vanishes, and, when the temperature has fallen to  $70^\circ$ , if the fluid be added by drops to a pure *solution of alloxan*, the latter is colored deep purple-red, and, in cooling, crystals of murexyd are deposited.

*Alloxanic Acid*:  $\text{HO}, \text{NC}_4\text{HO}_4$ . If to a warm so- Alloxanic acid.  
 lution of alloxan baryta water be gradually added, until the fluid begins to be turbid, alloxanate of baryta is thus separated. One atom of alloxan separates into 2 atoms alloxanic acid. From the baryta compound it is separated by gentle heat and by means of sulphuric acid. Crystallizes in small prisms; tastes sharply acid; easily soluble in water, and in 6 parts alcohol. If the aqueous solution be heated above  $60^\circ$ , carbonic acid is evolved, whilst leucoturic acid and difluan are formed. Warmed with nitric acid alloxanic acid is converted into parabanic acid. Alloxanic acid decomposes the carbonates and acetates, and dissolves zinc, whilst hydrogen gas is evolved. It forms *neutral, acid, and basic salts*; the neutral and the acid salts of the alkalis are soluble and crystallizable; the neutral salts of the alkali



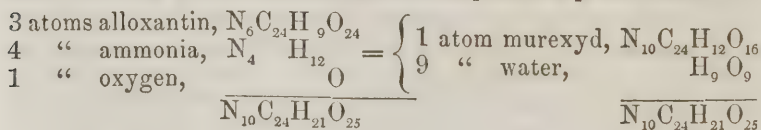
earths and of the heavy-metal oxides are not easily soluble; the acid salts, on the contrary, all dissolve easily. If their solutions are boiled, they separate into urea and *mesoxalates*.

*Thionuric acid.* *Thionuric Acid:*  $2\text{HO} + \text{N}_3\text{C}_8\text{H}_5\text{S}_2\text{O}_{12} = 2\text{HIO} + (\text{N}_3\text{C}_8\text{H}_5\text{O}_6)^{-} 2\text{SO}_3$ . If a solution of alloxan oversaturated with sulphurous acid be afterwards saturated with ammonia and then heated to boiling, after cooling, thionurate of ammonia is separated in shining leaflets. Thionuric acid is obtained when the salt, dissolved in water, is precipitated by acetate of lead, and the obtained precipitate is decomposed by hydrosulphuric acid. It appears as a very sour-tasting, crystalline mass; easily soluble in water. If the aqueous solution be boiled, it separates into sulphuric acid and uramil.

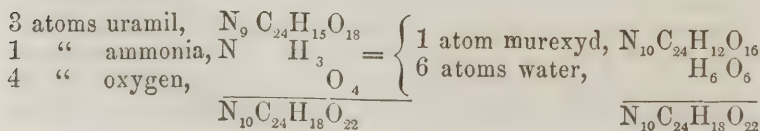
*Uramil.* *Uramil:*  $\text{N}_3\text{C}_8\text{H}_5\text{O}_6$ . Uramil is separated from the hot liquid in hard shining needles; insoluble in water, but easily soluble in ammonia. If it be warmed with *oxide of silver* or *oxide of mercury*, we obtain, by reduction of the oxides, alloxan, and murexyd. The ammoniacal solution of uramil, when exposed to the air, is colored at once rose-red, and if the solution be evaporated in the air, by absorption of oxygen, murexyd is formed. If to a solution of uramil and ammonia, alloxan be added, we obtain murexyd and dialuric acid. *Since a solution of uric acid in dilute nitric acid may contain alloxan and alloxantin, and the latter may, by presence of ammonia, be converted into uramil and alloxan, it is evident, that, when a solution of uric acid in nitric acid is saturated with ammonia, whether the air be admitted or not, murexyd must be formed.*

*Uramilic acid.* *Uramilic Acid:*  $\text{N}_5\text{C}_{16}\text{H}_{10}\text{O}_5$ . If uramil be boiled a long time with dilute sulphuric acid, in cooling, uramilic acid is separated in brightly shining prisms. 2 atoms of uramil plus 3 atoms water are equal to 1 atom uramilic acid and 1 atom ammonia.

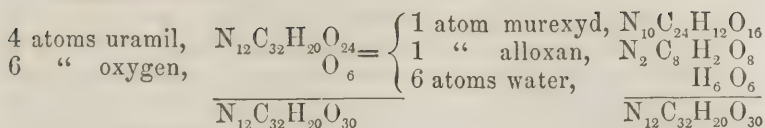
*Murexyd.* *Murexyd* (Purpurate of Ammonia):  $\text{N}_{10}\text{C}_{24}\text{H}_{12}\text{O}_{16}$ . This substance, together with alloxan, alloxantin, and uramil, which are the proximate cause of its formation, is the most wonderful product of the decomposition of uric acid. The following equations may serve to explain its production:—



Farther:—



Farther:—



We obtain murexyd: 1st. When equal parts uramil and oxide of mercury, diffused in 30 parts water, is slowly heated to boiling, whilst a few drops of ammonia are added; from the filtered solution murexyd is deposited in crystals; 2d. We evaporate, by exposure to the air, a solution of uramil in ammonia; 3d. We dissolve in boiling water 2 parts alloxantin and 3.5 parts aqueous alloxan, and when the temperature has fallen to 70°, we add to saturation carbonate of ammonia; after a few minutes crystals of murexyd are deposited; 4th. The solution of uric acid in dilute nitric acid, saturated with ammonia, is evaporated by gentle heat. Murexyd crystallizes in small, short, quadrilateral prisms; two surfaces reflect green light, like the sheath-wings of cantharides, both of the others show an intermingling of brown; by being rubbed, it is formed into a red powder, which, under the polishing iron, assumes a green metallic lustre. It is dissolved only in small quantity in water, with red color, and is insoluble in alcohol and ether. If the aqueous solution be boiled a short time, the murexyd is decomposed, whilst a yellow gelatinous substance is formed. If we lead hydrosulphuric acid into the solution, leaflets of murexan are precipitated, and the solution contains alloxantin and ammonia. If we drop nitrate of potassa into a boiling solution of murexyd, dark-red crystals of *purpurate of potassa* are separated. The *baryta compound* appears as a dark-green crystalline powder. Some chemists consider murexyd as an ammonia-salt, and give the formula  $\text{NH}_4\text{O} + \text{N}_5\text{C}_{16}\text{H}_4\text{O}_{10} + 2\text{aq}$ . The preceding formula is, at all events, to be preferred. If we add hydrochloric acid to murexyd, *murexan* is separated, and the solution contains alloxan, alloxantin, urea, and ammonia; a purpuric acid is in pure state unknown.

*Murexan* (Purpuric Acid):  $\text{N}_4\text{C}_{12}\text{H}_8\text{O}_{10}$ , appears as a very light silky lusted powder; easily soluble in alkalis. If the colorless, ammoniacal solution be evaporated by exposure to the air, murexyd remains. Murexan.

If *cafein* be decomposed by chlorine, we obtain, according to the duration of the action, several products in different proportions, which are directly allied to the products of uric acid. These products are *amelinic acid*, *murexoin*, and *cholestromphane*. Caffein, which is mentioned in connection with the organic bases, appears as a paired compound of hydrocyanate of methylamin with a substance,  $\text{N}_2\text{C}_{12}\text{H}_4\text{O}_4$ , which may be considered as uric acid, in Amelinic acid, murexoin, and cholestromphane.

which uren-imid is substituted by  $2C_2H_2$ ; hence its formula is  $(2C_2H_2)^-N_2C_8O_4$ . If with this substance the elements of 3 atoms of water + O combine, we obtain amelinic acid, which corresponds to alloxantin, and if ammonia and oxygen unite with amelinic acid, hence, in a similar way, arises murexoin, as murexyd from alloxantin. Cholestrophan is the compound corresponding to parabanic acid with  $2C_2H_2$ .

Alloxantin,  $N_2C_8H_3O_8 + 2C_2H_2 =$  Amelinic acid,  $N_2C_{12}H_7O_8$ .  
 Murexyd,  $N_{10}C_{24}H_{12}O_{16} + 6C_2H_2 =$  Murexoin,  $N_{10}C_{36}H_{24}O_{16} - HO$ .  
 Parabanic acid,  $N_2C_6H_2O_6 + 2C_2H_2 =$  Cholestrophan,  $N_2C_{10}H_6O_6$ .

*Amelinic Acid:*  $(2C_2H_2)N_2C_8H_3O_8$ . If the solution, which is formed by the action of chlorine upon caffen (when the latter is mixed with water and stirred to a paste) be evaporated, chlorine, hydrochloric acid, and chloride of cyanogen (?) escape, whilst at first crystals of amelinic acid are deposited, afterwards we obtain chloride of caffen, then cholestrophan, and in the mother-liquor hydrochlorate of methylamin is found. From the hot aqueous solution amelinic acid forms colorless, rather large crystals, which become rosy red when exposed to the air. If the solution be mixed with potassa and a salt of protoxide of iron, it becomes dark-blue; baryta water causes a blue precipitate; generally this substance shows all the reactions of alloxan.

*Murexoin:*  $(6C_2H_2)N_{10}C_{24}H_{12}O_{16} - HO$ . If amelinic acid, moistened with water, be exposed to the action of the air and vapor of ammonia, it is colored rose-red and finally brown. From the warm aqueous or alcoholic solution of this substance, in cooling, vermilion quadrilateral prisms are separated; two surfaces of these prisms reflect a golden-yellow color; if murexoin be rubbed with a polishing iron, it appears to have a metallic gold-lustre. The solution in water does not differ from that of murexyd.

*Cholestrophan:*  $(2C_2H_2)N_2C_6H_2O_6$ . From the hot alcoholic solution it crystallizes, whilst slowly cooling, in broad, silvery, colorless, transparent leaflets, an inch in length; they volatilize at  $100^\circ$ . If we boil it with potash-lye, we obtain, with evolution of ammonia, oxalate of potassa.

*Oxaluric Acid (Anabenic Acid):*  $HO, N_2C_6H_3O_7$ .  
 Oxaluric acid. The oxalurate of ammonia, which is formed when a solution of alloxantin in ammonia is evaporated by exposure to the air, is decomposed, in a warm solution, by sulphuric acid. By being quickly cooled, it separates as a crystalline powder, of very acid reaction; not easily soluble in water. It is also formed when parabanate of ammonia is evaporated by heat. If boiled a long time with water, it decomposes into 2 atoms of oxalic acid and 1 atom oxalate of urea.

*Dialuric Acid:*  $HO, N_2C_8H_3O_7$ . If into a boiling solution of alloxan or alloxantin hydrosulphuric acid

Dilauric acid.

be conducted so long as sulphur is deposited, and if we saturate with ammonia the liquid filtered from sulphur, after evaporating, dialurate of ammonia remains. By decomposing the salts with hydrochloric acid, we obtain the pure acid in crystals; it reacts acid; if the solution be long exposed to the air, allantoin arises, and if we heat it with ammonia, we obtain murexyd.

*Mykomelinic Acid*:  $N_4C_8H_5O_5$ . The ammonia salt of this acid is obtained when a solution of allo-Mykomelinic acid.  
xan in ammonia is heated. The salt, which is separated, is dissolved in hot water, and the solution mixed with hydrochloric acid. When dry, it appears as a yellow porous powder, not easily soluble in hot water; reddens litmus; gives no crystallizable salts.

*Allanturic Acid*:  $N_4C_{10}H_7O_9$ . Arises with allantoin when uric acid is decomposed with superoxide of Allanturic acid.  
lead. Also, when allantoin is heated to  $140^\circ$  with water in a tube closed by fusion. It is white, slightly acid, deliquescent, insoluble in alcohol.

*Hydurilic Acid*:  $2HO + N_3C_{12}H_3O_9$ , has only once been obtained by the action of dilute nitric Hydurilic acid.  
acid upon uric acid. A porous, white, crystalline powder; slightly soluble in cold water. With nitric acid it gives a white powder—nitrohydurilic acid  $= N_2C_8H_2O_{10}, NO_4(?)$ .

*Allituristic Acid*:  $HO, N_2C_6H_2O_3$ , is formed, when Allituristic acid.  
allantoin is quickly boiled with an excess of hydrochloric acid, and the residue treated with nitric acid. The allituristic acid, which remains behind, is separated from the boiling solution as a voluminous, crystalline, yellow powder; dissolves in 20 parts boiling water.

*Dilituric Acid*:  $2HO, N_3C_8HO_8$ , occurs in the Dilituric acid.  
nitric acid solution, which is obtained in the production of allituristic acid; by evaporating this solution, we obtain acid diliturate of ammonia in splendid, shining, yellow leaflets, from which the ammonia cannot be absorbed by an acid. Generally, the base cannot be completely withdrawn from the salts.

*Leucoturistic Acid*:  $N_2C_6H_3O_6$ , is obtained when the aqueous solution of alloxanic acid boils until it is Leucoturistic acid.  
evaporated to syrup-thickness, and the residue is treated with water. The acid remains as a snow-white, granulated, crystalline powder; insoluble in water; not attacked even by concentrated nitric acid. The ammonia salt crystallizes in needles; is soluble in water.

*Difluan*:  $N_2C_6H_5O_5$ . If the solution, poured off Difluan.  
from leucoturistic acid, be evaporated to syrup-thickness, and the residue be mixed with absolute alcohol, difluan is separated; when dried it appears as a brittle, gum-like, transparent mass, full of blisters; easily soluble in water; reacts slightly acid;



tastes saline, bitter, and is at once decomposed by potassa, whilst ammonia and oxalic acid are formed.

*Hidantoinic Acid*:  $\text{HO}, \text{N}_4\text{C}_8\text{H}_8\text{O}_8$ , is obtained when a solution of allantoin in concentrated potassal-ye is left to stand a few days. If the solution be over-saturated with acetic acid, the potassa-salt is separated as an oily liquid.

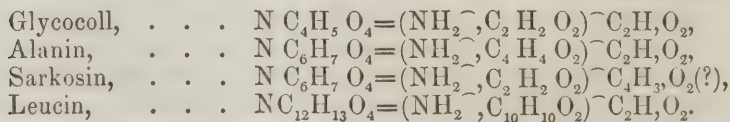
*Hyperuric Acid*(?):  $2\text{HO} + \text{N}_4\text{C}_{10}\text{H}_3\text{O}_7$ . If we mix 3 parts guanin with 5 parts chlorate of potassa, and add to the mixture 25 parts water and then 30 parts hydrochloric acid; when the mixture is warmed to  $25^\circ$ , there are formed, after two hours, crystals of hyperuric acid. It crystallizes in short, rhombic prisms with oblique end-surfaces; shining, colorless, tasteless, and inodorous; reddens litmus; not easily soluble in water and acids, but easily so in alkalies. By being heated to redness, it gives a large quantity of cyanic acid.

*Xanthic-oxyd*. *Xanthic-oxyd* (Uric-oxyd, Xanthine):  $\text{N}_2\text{C}_5\text{H}_2\text{O}_{22}$ , is occasionally found in human urinary calculi. The calculi, consisting of xanthic-oxyd, are light brown, smooth, and shining; and consist of concentric separable layers.

*Rosacic acid*. *Rosacic Acid* is occasionally found in the roseate sediment which in some diseases is deposited from the urine. This red substance is dissolved in boiling alcohol, and remains, after evaporation, as a vermilion, inodorous substance, scarcely acid reacting; soluble in water and alcohol. With the alkalies it forms soluble salts. Sulphuric acid precipitates it with dark-red color. Nitric acid is said to convert it into uric acid.

## ORGANIC ALKALIDS.

As organic alkalids, I designate a few organic combinations, which in a certain measure make the transition from the nitrogen combinations above treated, and the so-called organic bases, which will be described in the following part. These combinations are especially distinguished by the fact, that they behave indifferently, and unite with bases, acids, and salts, without destroying the chemical properties of these substances. They essentially differ from the amid-combinations, inasmuch as, when warmed with aqueous alkalies, they evolve no ammonia. They all contain oxygen, and are probably paired amid-compounds with organic acids (*see* page 82). Several of them form an ascending series with the difference:  $\text{C}_2\text{H}_2$ , *e. g.*



*Glycocoil* (Gelatine-sugar):  $\text{NC}_4\text{H}_5\text{O}_4 = (\text{NH}_2\text{C}_2\text{H}_2\text{O}_2)\text{C}_2\text{H}_3\text{O}_2 = (\text{NH}_3\text{C}_2\text{HO}_3)\text{C}_2\text{H}_3\text{O}$ . This substance forms the pairing of hippuric acid, cholic and choleinic acid; it <sup>Glycocoil.</sup> is formed by the action of sulphuric acid or potassa upon glue and the protein-compounds, as flesh, etc. Glue is boiled a long time with potash-lye, neutralized with sulphuric acid, evaporated, the residue treated with alcohol, which dissolves glycocoil and leucin; the two substances are separated by spontaneous evaporation; first, leucin crystallizes, and then glycocoil. Or, we boil hippuric acid a long time with from 6 to 8 parts moderately dilute hydrochloric acid, remove the benzoic acid, which is separated in cooling, and evaporate the solution of hydrochlorate of glycocoil; then we saturate to excess the residue with ammonia and mix it with alcohol; after a short time glycocoil is separated as a crystalline substance. It forms large, hard, colorless crystals of the oblique, rhombic system (des 2—1 gliedrigen Systems); dissolves in 3 to 4 parts cold water, more easily in boiling; tastes sweet; bears the action of the air; melts and decomposes in a higher temperature. By the action of chlorine it is converted into a peculiar acid. If it be fused with hydrate of potassa, at the commencement it is colored fiery-red; ammonia is evolved, whilst cyanide of potassium and oxalate of potassa remain as residue.

*Sulphate of Glycocoil*:  $\text{NC}_4\text{H}_4\text{O}_3\text{SO}_3(?)$ , is obtained when sulphuric acid is added by drops to an alcoholic solution of glycocoil, after a little time shining crystals are separated in the cold; after the addition of the sulphuric acid, if we heat the solution to boiling, we sometimes obtain crystals consisting of  $\text{NC}_4\text{H}_5\text{O}_4\text{SO}_3$ ; both combinations taste very sour and are easily soluble in water.

*Nitrate of Glycocoil*:  $\text{NC}_4\text{H}_5\text{O}_4 + \text{HO,NO}_5$ , forms large transparent, rhombic crystals, which are soluble in water, but not in alcohol. It is obtained by dissolving glycocoil in cold dilute nitric acid, and cautiously evaporating the solution.

*Hydrochlorate of Glycocoil*:  $\text{NC}_4\text{H}_5\text{O}_4\text{HCl}$ , is obtained when hippuric acid is boiled a short time with hydrochloric acid. Forms transparent, shining, long crystals; tasting slightly acid.

*Glycocoil-potassa*. If the solution of glycocoil in dilute potassa be evaporated upon the water-bath to syrup-thickness, we thus obtain deliquescent, very alkaline reacting needles.

*Glycocoil-leadoxyl*:  $\text{PbO,NC}_4\text{H}_5\text{O}_4$ , is obtained when oxide of lead is boiled with an aqueous solution of glycocoil, and the filtrate mixed with alcohol, until it becomes turbid; after standing long, the compound crystallizes similarly to cyanide of mercury.

*Glycocoil-copperoxyd*:  $\text{CuO,NC}_4\text{H}_5\text{O}_4$ , crystallizes in beautiful blue needles.

*Glycocoil-sulphate of Potassa*. If to a mixture of glycocoil and acid sulphate of potassa, dissolved in water, alcohol be added,

we obtain transparent needles, which consist of  $2\text{NC}_4\text{H}_4\text{O}_3, \text{KO}, 2\text{SO}_3$ .

*Glycocoll-nitrate of Potassa*:  $\text{NC}_4\text{H}_4\text{O}_3, \text{KO}, \text{NO}_5$ . This substance is precipitated when alcohol is added to an aqueous solution of glycocoll and nitrate of potassa. The compounds of glycocoll with the acids behave like paired acids, and, with the bases, give salts soluble in water, in which it may also be assumed that glycocoll takes the place of water of crystallization.

*Alanin*.  $\text{NC}_6\text{H}_7\text{O}_4 = (\text{NH}_2, \text{C}_4\text{H}_4\text{O}_2) \text{C}_2\text{H}_2\text{O}_2$ . If we add hydrocyanic acid to a solution of aldehyd-ammonia, and evaporate the solution with hydrochloric acid, we thus obtain a residue of hydrochlorate of alanin and chloride of ammonium, which substances are separated by a mixture of alcohol and ether. The hydrochlorate of alanin, by being boiled with hydrated oxide of lead in an alcoholic solution is decomposed. From alcohol it crystallizes in colorless, hard, tufted prisms, of pearly lustre, which dissolve in 4.6 parts water, but only with difficulty in alcohol; insoluble in ether. The solution tastes very sweet; alanin sublims at  $200^\circ$ . If we warm the aqueous solution with superoxide of lead, it separates into carbonic acid, aldehyd, and ammonia. It can be boiled with dilute acids and alkalies, without suffering decomposition. If we conduct nitrous acid into the aqueous solution of alanin, we obtain lactic acid (see page 143), whilst nitrogen gas is evolved. Like glycocoll alanin unites with acids and bases; whether it can also unite with salts is doubtful.

*Sarkosin*.  $\text{NC}_6\text{H}_7\text{O}_4$ . This compound, which is isomeric with alanin, is obtained when kreatin is boiled with baryta water (v. Kreatin) so long as ammonia escapes, and by leading carbonic acid into a solution filtered from carbonate of baryta, the baryta is precipitated. After evaporating the solution, we obtain sarkosin in water-clear, direct, rhombic columns, which are much more easily soluble in water than alanin; not easily soluble in alcohol, insoluble in ether; sublims at  $100^\circ$ ; tastes sweet, and, at the same time, metallic. It combines like alanin with acids, but not with bases. The combinations with the acids react acid.

*Leucin*.  $\text{Leucin}$  (Aposepidin):  $\text{NC}_{12}\text{H}_{13}\text{O}_4 = (\text{NH}_2, \text{C}_{10}\text{H}_{10}\text{O}_2) \text{C}_2\text{H}_2\text{O}_2$ . It is formed simultaneously with glycocoll by the action of sulphuric acid or potassa upon glue and the protein substances (see above *Glycocoll*). From the aqueous solution it crystallizes in pearly scales, which dissolve in 27.7 parts cold water, and in 658 parts alcohol; in ether they are insoluble. It is tasteless, inodorous; indifferent. Fused with hydrate of potassa, we obtain valerianate of potassa (whilst ammonia and hydrogen gas are evolved), and in higher temperature also butyric acid. It

combines with acids like alanin; nitrate of leucin appears in small acid-tasting crystals.

*Taurin*:  $\text{NC}_4\text{H}_7\text{S}_2\text{O}_6 = (\text{NH}_3^+, \text{C}_4\text{H}_4\text{O}_2)^- 2\text{SO}_2$ . This *Taurin*. substance occurs as pairing of choleinic acid in the gall of the ox, and of other animals. We let oxgall, at a temperature of 30 to 37° stand for three weeks, or until it reacts clearly acid, then precipitate with acetic acid, filter and evaporate the filtrate to dryness. The residue is first extracted by alcohol, and the remaining undissolved part dissolved in boiling water. From the evaporated solution taurin appears in large water-clear crystals; destitute of taste and smell; they dissolve in 15.5 parts cold water; completely indifferent; not volatile; in the cold it is not decomposed by chlorine. If we slowly evaporate taurin in potassa solution, at a fixed point of concentration, ammonia instantaneously escapes, and the residue contains sulphate and acetate of potassa; in this no blackening is observed. If we conduct sulphurous acid into aldehyd-ammonia, we obtain a substance of the same constitution.

*Cystin* (Cystic Oxide):  $\text{N}_2\text{C}_6\text{H}_6\text{S}_2\text{O}_4$ . This body is *Cystin*. sometimes found in urinary calculi and in the kidneys. Crystallizes in hexagonal, colorless, transparent leaflets, which are hardly soluble in water; but easily soluble in dilute acids, with which it gives crystallizable compounds. When boiled with baryta water, we obtain sulphide of barium, and a yellow substance.

*Tyrosin*:  $\text{NC}_{18}\text{H}_{11}\text{O}_5$ . If we boil fresh pressed *Tyrosin*. cheese, or other protein matter, with a most highly concentrated solution of potassa, until hydrogen gas, as well as ammonia, escapes, then dissolve the mass in hot water, and oversaturate with acetic acid, in cooling, white silky needles are separated. Tyrosin, like glycocoll, unites with acids as well as with bases; not easily soluble in water. If we treat tyrosin with strong nitric acid, we obtain *nitrate of nitrotyrosin*:  $\text{NC}_{18}\text{H}_{10}\text{O}_6$ ,  $\text{NO}_4 + \text{NO}_5$ .

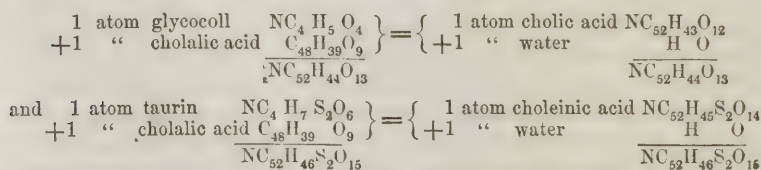
*Kreatin*:  $\text{N}_3\text{C}_8\text{H}_9\text{O}_4 = (\text{NC}_2\text{H}, \text{NH})^+ \text{NC}_6\text{H}_7\text{O}_4^-$ . *Kreatin*. This is found in the muscular fibre of the mammalia, birds, amphibials, and fishes, yet only in small quantity. Clean flesh, freed from fat, and cut in small pieces, is kneaded thoroughly with water, and then pressed out. The liquid is warmed until the albumen and crassamentum are coagulated, then it is filtered, and the filtrate mixed with baryta water so long as a precipitate of phosphate of baryta and of magnesia is produced; we afterwards filter and evaporate the filtrate in a flat bowl upon the water bath to 1-20th, the residue is then left in a cool place a long time. Crystals of kreatin form, which, by being repeatedly crystallized, treated with animal charcoal, etc., are purified. From the aqueous solution it crystallizes in water-clear, shining,



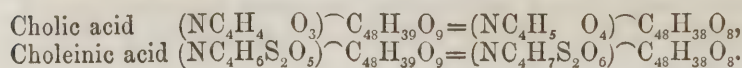
oblique, rhombic columns, containing 2 atoms of water of crystallization, which they lose at  $100^{\circ}$ . Easily soluble in boiling water, in 74.6 parts cold water, and in 2000 parts alcohol, insoluble in ether, inodorous, almost tasteless, non-volatile. If we boil 1 part kreatin with 20 parts crystals of baryta and water, it separates into urea and sarkosin. One atom kreatin + 2 atoms water give 1 atom urea and 1 atom sarkosin. According to the above formula, kreatin consists of sarkosin and uren-imid, which, with the elements of 2 atoms of water, is converted into urea, but that at once decomposes into carbonic acid and ammonia. Hence kreatin may be compared to uric acid. If kreatin be boiled with strong *hydrochloric acid*, by the loss of  $2\text{H}_2\text{O}$ , it is converted into a base—*kreatinin*.

*Inosinic acid.* *Inosinic Acid:*  $\text{HO}, \text{N}_2\text{C}_{10}\text{H}_6\text{O}_{10}$ . If we farther evaporate the mother-liquor of flesh extract, out of which kreatin is crystallized, and if we then gradually add alcohol until the liquid begins to grow turbid, we obtain, after a short time, crystals, which principally consist of inosinate of potassa, or of baryta. These crystals are dissolved in hot water, and the solution is mixed with chloride of barium; it is then filtered; after cooling, we obtain inosinate of baryta, which is decomposed by sulphuric acid. After the evaporation of the aqueous solution, we obtain inosinic acid, as a syrup-like mass, which, by being treated with alcohol, becomes solid. Inosinic acid tastes like meat broth, and gives an acid reaction. The *potassa salt* crystallizes in long quadrilateral prisms. The *soda salt* in silky needles; both salts are easily soluble in water. The *baryta salt* appears in long quadrilateral leaflets, of mother-of-pearl lustre; they dissolve in 400 parts cold water. The *copper salt* is an insoluble light-blue powder.

*Paired acids of glycocoll and taurin.* *Cholic Acid and Choleinic Acid.* As hippuric acid, by being boiled with hydrochloric acid, decomposes into glycocoll and benzoic acid, so is cholic acid, by the action of acids and alkalies, converted into glycocoll and cholalic acid (*see p. 278*) and choleinic acid into taurin and cholalic acid. For instance:—



Hence both combinations belong to the paired acids; therefore their formulæ are:—



Both acids occur as potassa salts, in the gall, of which they are the main constituents.

*Cholic Acid*:  $(\text{NC}_4\text{H}_4\text{O}_3) \cdot \text{C}_{43}\text{H}_{39}\text{O}_9$ . We add sugar of lead to fresh oxgall, extract the obtained precipitate with cold alcohol, conduct hydrosulphuric acid into the solution, filter from the sulphide of lead, and add water to the filtrate until it begins to be turbid; after standing a long time, cholic acid is separated in crystals. Or we extract with absolute alcohol, the gall entirely dried at  $100^\circ$ , filter, and add ether to the filtrate in small quantities, so long as a brown resinous precipitate arises (which is principally choleinate of soda). Now we pour off the liquid from the precipitate, and leave it to stand a long time, excluding the air. It forms shining tufts of crystals, which are at once washed with alcohol and ether, and dried in vacuum over sulphuric acid. These crystals are real cholate of soda. If they are dissolved in water, the solution precipitated with acetate of lead, the precipitate decomposed by carbonate of soda, evaporating the solution, and extracting the residue with absolute alcohol, whilst we add ether to the alcoholic solution, we thus obtain pure cholate of soda, from which the pure cholic acid is precipitated by sulphuric acid. Cholic acid forms fine white needles, destitute of a fixed crystal form; they taste bitter-sweet, and suffer no change at  $120^\circ$ . It dissolves in 121 parts hot water, and in 303 parts cold, is easily dissolved in alcohol; if we evaporate the alcoholic solution, cholic acid remains, like resin, behind; but if we mix the solution with water or ether, it separates gradually into crystals; it is hardly soluble in ether; sulphuric acid, hydrochloric acid, and acetic acid absorb it without causing it to decompose. The solution of cholic acid reacts acid. *Ammonia*, *potassa*, *soda*, and *baryta water* dissolve it abundantly, and it is precipitated by acids, like a resin. The salts of *lime*, *baryta*, *strontia*, and *magnesia*, cause no precipitate in the solution of the acid. Sugar of lead causes a flocculent precipitate, and, if we add vinegar of lead to the abfiltered liquid, yet again a precipitate is formed. *Perchloride of iron* produces a yellow precipitate and *nitrate of silver* a gelatinous one; all cholates are soluble in alcohol.

*Paracholic Acid*. If the aqueous solution of cholic acid be boiled a long time with water, it becomes insoluble, and then appears in leaflets of mother-of-pearl lustre, which exhibit six-sided plates. From the alcoholic solution common cholic acid is again separated.

*Paracholic acid* as well as *cholic acid* give the same reactions with *sugar* and sulphuric acid, as were described in cholalic acid (see page 278). *Cholate of soda* is obtained, when we saturate cholic acid with carbonate of soda, evaporate the solution, extract the residue with alcohol, and add ether to the solution. It forms

stellated white needles, which are easily soluble in water and alcohol; melts by warming, burns with a sooty flame, and leaves an alkaline reacting residue, which contains much cyanate of soda.

*If we boil cholic acid from 12 to 24 hours with baryta water, it separates into glycocholl and cholalic acid. It also suffers the same decomposition by being boiled with hydrochloric acid, only the cholalic acid is easily converted into choloidinic acid and dyslysin (compare Cholalic Acid, p. 278).*

**Choleinic acid.** *Choleinic Acid:*  $\text{HO}, (\text{NC}_4\text{H}_6\text{S}_2\text{O}_5)^- \text{C}_{48}\text{H}_{39}\text{O}_9$ . This acid has not been obtained perfectly pure. If we add vinegar of lead to gall, after the cholic acid has been precipitated by neutral acetate of lead, the precipitate consists for the most part of choleinate of lead, yet always mixed with cholate of lead. The resinous mass, which, in the commencement, is precipitated by the addition of ether to the alcoholic solution, contains principally choleinic acid. The acid does not appear to crystallize. In water, it is more easily soluble than cholic acid, and is a stronger acid than that; it dissolves fats, fatty acids, and cholesterin in considerable quantity, and prevents the precipitation of cholic acid in the gall, by acetic acid and mineral acids. The alkaline salts are easily soluble in water and alcohol, and in ether are insoluble; they taste bitter-sweet; deliquesce in the air, and, by being a long time treated with ether, become crystalline. Acids produce no precipitate in the solutions; on the contrary, the salts are precipitated by concentrated *potash-lye*. The salts of *lime*, *baryta*, and *magnesia*, as well as *neutral acetate of lead*, do not produce a precipitate. On the contrary, vinegar of lead causes a plaster-like precipitate, which is dissolved by being warmed, as well as by an excess of vinegar of lead. Acetate of copper causes, only in the presence of ammonia, a bluish-white precipitate, soluble in ammonia. Nitrate of silver is not precipitated, not even in the presence of ammonia; as also corrosive, *sublimite*. *Nitrate of protoxide of mercury* and *protochloride of tin* produce a white flocculent precipitate. By heating with *sugar* and *sulphuric acid*, a violet color is produced.

**Hyochohic acid.** *Hyochohic Acid:*  $\text{HO}, (\text{NC}_4\text{H}_4\text{O}_3)^- \text{C}_{50}\text{H}_{41}\text{O}_9$ . This acid differs from cholic acid by a plus of  $\text{C}_2\text{H}_2$ . It occurs in the gall of swine. If we mix fresh swine's gall with a solution of *Glauber's salts*, dissolve the precipitate which is formed in absolute alcohol, and mix the solution with ether, the soda salt is deposited, and is decomposed by sulphuric acid. The precipitated acid is dissolved in alcohol and precipitated from the alcoholic solution by water. It appears as a white, resinous mass, which completely dry, melts at  $120^\circ$ ; slightly soluble in water, insoluble in ether, easily soluble in alcohol, concentrated sulphuric acid, and nitric acid. A very durable acid, which, by being boiled a long time with concentrated sulphuric acid, is decomposed into

glycocoll and an acid corresponding to cholalic acid. Treated with *fuming nitric acid*, it gives cholesterinic, benzoic, butyric acid, etc., in the same manner as by chromic acid. The alkaline salts are easily soluble in water and alcohol; they taste bitter, redden litmus, and are withdrawn from their aqueous solution by alkaline salts. The precipitate contains the base of the added salts. With salt of *baryta*, *lime*, and *magnesia*, they give *white* precipitates, which dissolve in warming. The *heavy metal-salts* are insoluble in water, but in alcohol, on the contrary, they are soluble. The salts do not possess the property of crystallizing.



## FIFTH DIVISION.

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### HYDRYLS.

#### ORGANIC SALT BASES.

Simple organic bases. BY organic salt bases (alkaloids), in the narrowest sense, are understood especially the organic compounds, which agree in their chemical relations with ammonia, and, to the oxides of methyl, ethyl, and amyl, stand in a similar relation as ammonia towards the basic oxides of the metals. Ammonia is the prototype of all organic bases. As was said in the General Part of this work, all the radicals of the methyl and benzid group possess the property to replace, wholly or partially, the hydrogen in ammonia, and thus to form basic compounds, which, in all respects, agree with ammonia. As in these bases the hydrogen of ammonia is substituted by organic radicals, so can also the nitrogen of the same be replaced by phosphorus, arsenic, and antimony. Thus ammonia,  $\text{NH}_3$ , corresponds to hydro-antimony,  $\text{StH}_3$ , and triethylamin,  $\text{NAe}_3$ , to stibethyl,  $\text{StAe}_3$ . If to stibmethyl,  $\text{StMe}_3$ , we add iodide of methyl, we obtain a salt,  $(\text{StMe}_4)\text{I}$ , corresponding to iodide of ammonium,  $(\text{NH}_4)\text{I}$ . If we treat the iodine compound with oxide of silver, we obtain a base,  $(\text{StMe}_4)\text{O}$ , which agrees in all properties with potassa. All bases of this group possess the property of forming metal-like bodies with  $\text{H, Me, Ae}$ , etc. (which bodies are closely allied to the alkaline metals), and of producing compounds endowed with all the characteristics of inorganic salts. In this respect they are essentially distinguished from the salt-like compounds of methyl, ethyl, etc., in their free state. Kakodyl,  $\text{As Me}_2$ , possesses the same character as the compounds with 4 atoms,  $\text{H, Me, Ae}$ ; it behaves quite like a metal, and gives, with 1 atom oxygen, a base corresponding to the metal oxides. If upon stibmethyl or stibethyl we let iodide of methyl or iodethyl act, we obtain, as already remarked, compounds  $= \text{StMe}_3 + \text{I}$  and  $\text{StAe}_3 + \text{I}$ . But if we bring these bodies together with chlorhydrogen, thus is hydrogen separated and salts are formed consisting of  $\text{StMe}_3 + \text{Cl}_2$ ,

and  $\text{StAe}_3 + \text{Cl}_2$ , whilst chlor-kakodyl is formed of  $\text{AsMe}_2 + \text{Cl}$ . In the General Part, it was supposed that kakodyl consists of  $(\text{AsMe})^-\text{Me}$  and stibethyl of  $(\text{StAe})^-\text{Ae}_2$ . But if we consider kakodyl as a radical like ammonium, then stibethyl appears as a double radical consisting of  $\text{Ae} + \text{StAe}_2$ . Chlorstibethyl then consists of  $(\text{StAe}_2)\text{Cl} + \text{AeCl}$ , and oxide of stibethyl is a double base  $= (\text{StAe}_2)\text{O} + \text{AeO}$ . All bases of this group form the class of *simple organic bases*, which may be divided into *nitrogen bases*, *phosphorous bases*, *arsenic bases*, and *antimony bases* (see page 79).

If organic bodies unite as pairlings with the simple bases, thus arises the class of *paired organic bases*, of which those only of the nitrogen bases are known. In most cases, it is with ammonia that the pairling combines; however, it is very probable that with the other nitrogen bases pairlings may join. Since the simple bases are almost all volatile, but most of the paired are not, therefore we divide also the organic bases into the *volatile* and *non-volatile*. Paired bases.  
Volatile and non-volatile bases.

### First Group.

#### NITROGEN BASES.

The organic bases occur in the vegetable kingdom, especially in those plants and parts of plants, which are distinguished by their action upon the animal organization, as the narcotic and poisonous; they are always united to the organic acids. Several simple bases are formed simultaneously with ammonia in the dry distillation of nitrogenous bodies, and are found also in tar oil. Upon the formation of these bases out of the nitro-compounds of the benzid group, we refer to the General Part (page 81); in the same place are also given the most important facts upon the formation of the bases of methyl, ethyl, and amyl. Paired bases, as urea, amarin, furfuran, thiosinamin, etc., can also be artificially obtained. Occurrence and formation of nitrogen bases.

#### SIMPLE NITROGEN BASES.

Most of the simple organic bases are artificially obtained; at common temperature they appear gaseous, fluid, or solid; the simpler their constitution is, the more volatile are they; in a gaseous state they all correspond to 4 volumes. In basic characteristics many of them exceed ammonia; the gaseous are absorbed by water in uncommonly great quantity; the fluid are easily soluble in water, alcohol, and ether. They possess a strong, often ammoniacal, benumbing smell, and most of them a sharp, caustic, and bitter taste. Like ammonia, A few general properties of simple bases.

they give, with acids, compounds like imidic, amidic, and aminic acid, and all have the property of forming with chloride of platinum double acids, corresponding to platinum-chloride of ammonium. If these bases combine with acids, 1 atom of H, Me, Ae, etc., also enters the base, and forms a body corresponding to ammonium, which, with O, forms the oxygen base, and with the halogens the corresponding haloid compounds. In the following, only the most important relations of these bodies can be given.

*Ammonia*,  $\text{NH}_3$ , and *ammonium*,  $\text{NH}_4$ , whose compounds are supposed to be known.

#### BASES OF THE METHYL GROUP.

The bases of the methyl group may be considered as ammonia, in which 1, 2, or 3 atoms of H are replaced by an equal number of atoms of methyl, ethyl, etc.

Their production. The compounds which contain 1 atom of an organic radical, are formed,

1st. When cyanate or cyanurate of methyl, ethyl, or amyl is boiled with potash lye, whilst simultaneously carbonate of potassa is formed.

2d. By the action of the iodine and bromine compounds of the said radicals upon ammonia. If, for example, 1 atom of bromide of methyl acts upon 1 atom of ammonia, we obtain  $(\text{NH}_2\text{Me})\text{Br}$ . If we distil this compound with potassa, there are formed bromide of potassium, water, and  $\text{NH}_2\text{Me}$ . Afterwards, if we let bromide of methyl act upon this body, there arises  $(\text{NH}_2\text{Me}_2)\text{Br}$ , and through decomposition with potassa, it forms bimethylamin,  $\text{NHMe}_2$ , which, by being farther treated with bromide of methyl, is converted into  $\text{NMe}_3$ , and, finally, into  $\text{NMe}_4$ . In like manner, by varying the action of bromide of methyl, bromide of ethyl, and bromide of amyl upon ammonia, we obtain bases in which the hydrogen is simultaneously replaced by methyl, ethyl, and amyl.

3d. If we lead ammonia gas into neutral sulphate of ethyl, we obtain an ammonia salt, which corresponds to the formula  $\text{NH}_3 + 4(\text{C}_4\text{H}_5\text{O}) + 4\text{SO}_3$  (ethamin-sulphate of ammonia). If we boil this compound with carbonate of baryta, until no more ammonia is evolved, and add potash lye, ethyl-amin distils over. If upon the hydrochlorate of methyl, ethyl, or amyl-amin, nitrate of silver acts, we obtain, with evolution of nitrogen gas, nitrite of methyl, ethyl, or amyl.

*Methyl-amin*:  $\text{NH}_2\text{Me}$ . This base is also formed by the decomposition of caffen by chlorine (*see* Caffen), as also by heating morphine with an excess of hydrate of potassa. A colorless gas; smells like ammonia; sp. gr. 1.13; is fluid at  $0^\circ$ ; 1 volume of water absorbs at  $12^\circ$ , 1040 volumes gas,

and forms a strong caustic liquid. Chemically, it behaves quite like ammonia. The hydrochloric acid salt,  $(\text{NH}_3\text{Me})\text{Cl}$ , crystallizes in leaflets of mother-of-pearl lustre, which easily dissolve in water. In contact with potassium, it gives cyan-potassium and hydrogen gas,  $\text{NH}_2\text{C}_2\text{H}_3 + \text{K} = \text{KNC}_2 + 5\text{H}$ .

*Ethyl-amin*:  $\text{NH}_2\text{Ae}$ , is entirely like the preceding compound; dissolves in somewhat lesser quantity in water. *Dicethyl-amin*,  $\text{NHAe}_2$ , is a colorless, strongly alkaline fluid; soluble in water in greater quantity. The bromine-compound,  $(\text{NHAe}_2\text{H})\text{Br}$ , crystallizes in yellow needles. *Triethyl-amin*,  $\text{NAe}_3$ , resembles the preceding compound; is very combustible. The bromine compound  $(\text{NAe}_3\text{H})\text{Br}$ , crystallizes and in contact with bromide of ethyl goes over into tetra-ethylamin,  $(\text{NAe}_4)\text{Br}$ . From this salt, by treating with oxide of silver, the base,  $(\text{NAe}_4)\text{O}$ , can be obtained. It entirely agrees with potassa.

*Propyl-amin*:  $\text{NH}_2\text{C}_6\text{H}_7$ , is obtained when narcotin is heated to  $220^\circ$  with an excess of hydrate of potassa. Strongly alkaline, smells like ammonia; easily soluble in water. The hydrochloric acid solution gives with chloride of platinum, a pale yellow precipitate. Treated with nitrite of potassa, it gives, probably, with evolution of nitrogen gas  $(\text{C}_6\text{H}_7)\text{O}, \text{NO}_3$ .

*Butyl-amin* (Petenin):  $\text{NH}_2\text{C}_8\text{H}_7$ , occurs in the so-called Dippel's oil, which is obtained by distilling bones, and in the most volatile portion of it. We treat the latter a long time with dilute sulphuric acid, evaporate the sulphuric acid solution, and distil the residue with an alkali. We obtain a mixture of different bases, which are separated by fractional distillation. At  $80^\circ$  butylamin goes over; finally, we obtain *anilin*. Butylamin is transparent, colorless, strongly refracts light; of unpleasant odor; tastes sharply burning; is soluble in all proportions in water, alcohol, and ether. Precipitates the salts of oxide of iron and oxide of copper. The latter oxide is redissolved in an excess of the precipitant with a blue color. The salts can be crystallized; do not change in the air, and are sublimable, if the acid be volatile. The neutral sulphuric acid salt becomes moist in the air, forming acid salts. With chloride of mercury and of platinum, it forms soluble salts; with chloride of gold, it forms an insoluble compound.

*Amyl-amin*:  $\text{NH}_2\text{C}_{10}\text{H}_{11}$ , a fluid of ammoniacal smell, and burning bitter taste. The chlorine compound,  $(\text{NH}_2\text{Am}, \text{H})\text{Cl}$ , crystallizes in white unctuous scales.

*Methyl-ethylamin*:  $\text{NHMeAe}$ , *Methyl-biethylamin*:  $\text{NMeAe}_2$ , *Methyl-amylamin*:  $\text{NHMeAm}$ , *Ethyl-amylamin*:  $\text{NHAeAm}$ , *Biethyl-amylamin*:  $\text{NAe}_2\text{Am}$ , etc., and their oxides, are obtained in the manner above described.

*Chloro-nicin*:  $\text{NH}_2(\text{C}_{10}\text{H}_2\text{Cl})$ , is obtained by the action of hydrosulphuric acid upon nitrochlornicid.



*Benzidin* :  $\text{NHBd}=\text{NH}, \text{C}_{12}\text{H}_{15}=(\text{NH}_2, \text{C}_{12}\text{H}_5)+$   
 Bases of the (NH<sub>2</sub>, C<sub>12</sub>H<sub>5</sub>), is obtained from azobenzid, as anilin  
 benzid group. from nitrobenzid (*vide* below). In a pure state, it  
 Benzidin. crystallizes in dazzling white silvery scales; slightly  
 soluble in cold water, easily, in boiling, as also in alcohol and  
 ether; odorless; taste, biting alkaline; melts at 108°. By dis-  
 tillation, it partially decomposes. With acids, it forms white, fine,  
 crystallizable salts, which are enduring. If we lead chlorine into  
 the solution of the salts they are, at first, colored blue, then red-  
 dish-brown, and finally are separated, as a crystalline vermilion  
 powder. Dilute solutions of these salts give, with sulphuric acid,  
 a precipitate.

Picolin.

*Picolin* (Odorin):  $\text{NH}_2, \text{C}_{12}\text{H}_5$ . It occurs, in com-  
 mon with butylamin, in Dippel's oil, as also in coal-  
 tar oil, and in each part thereof which, in distillation, goes over  
 first, together with anilin. It is more volatile than anilin, less so  
 than butylamin, and can be separated by fractional distillation.  
 What goes over at 133° is pure picolin. It arises, farther, by the  
 decomposition of piperins (which see), colorless, very mobile, thin-  
 flowing liquid, of strong, penetrating, somewhat aromatic smell,  
 and sharp, burning, bitter taste. Still fluid at -17°, boils at  
 133°; sp. gr. 0.955. Mixes with water, alcohol, and ether, in all  
 proportions. Is not precipitated by solution of chloride of lime,  
 does not coagulate albumen, reacts alkaline. Nitrate of silver,  
 chloride of barium, chloride of strontium, and sulphate of mag-  
 nesia, are not precipitated by picolin. Tannin causes a white,  
 cheesy precipitate. It combines with the chlorides of mercury,  
 platinum, tin, and antimony. If we add picolin to a solution of  
 chloride of gold, we obtain fine lemon-colored needles. The salts  
 possess the property of crystallizing.

Anilin.

*Anilin* (Benzidam, Kyanol, Krystallin):  $\text{NH}_2\text{Bd}$   
 $=\text{NH}_2, \text{C}_{12}\text{H}_5$ . This base, which has the same consti-  
 tution as picolin, occurs in coal-tar oil, as well as in Dippel's oils.  
 That which, by fractional distillation of the mixed bases, goes  
 over at 182°, is anilin. It is farther formed by heating anthra-  
 nilic acid.

If, into the alcoholic solution of nitrobenzid, saturated with  
 ammonia, we lead sulphide of hydrogen, sulphur is separated,  
 and shortly the whole stiffens, at 0°, to a mass consisting of yellow  
 crystalline needles. If this be heated to boiling, the solution fil-  
 trated away from the sulphur, and the filtrate distilled until the  
 contents of the retort separate into two layers, then is the lower  
 one *anilin*, which is purified by distillation. It is a colorless  
 fluid, strongly refracts light, has a penetrating odor, taste sharply  
 burning, sp. gr. 1.020, boiling point 182°, easily soluble in cold  
 water, alcohol, and ether; if the aqueous solution be warmed, it  
 clouds, and a portion of anilin is separated; reacts not alkaline,

coagulates albumen. In contact with hydrochloric acid it forms a white vapor. If to a solution of chloride of lime we add anilin, a deep violet-blue color is formed, which, when acids are added, becomes deep red. By these reactions, anilin is distinguished from the other bases which have the same constitution. With the acids, anilin forms crystallizable inodorous salts, which are soluble in water and in alcohol, and which, in the moist air, soon become rosy-red. Anilin precipitates the salts of protoxide and peroxide of iron, alumina, and oxide of zinc. Cyanide of potassium, ferrocyanide of potassium, and sulphocyan-potassium do not react upon salts of anilin; tannin causes a brown precipitate.

*Anilids and Anilic Acids.* Under Anilids we understand the compounds corresponding to the amidic acids, and under anilic acids those compounds corresponding to the aminic acids, of which compounds a great number are known. These compounds are mostly solid, and crystallizable. The anilic acids saturate 1 atom, base. They are nearly all obtained when anilin is heated with an excess of pure acids. The anilic acids are, in part, soluble in water; whilst anilid remains behind. If we treat these compounds in the heat with dilute potash lye, we obtain anilin and the original acids. Under anilic acids are often also understood the acid salts of anilin, if they possess the property to form salts with the bases. If upon anilin we let nitrous acid act, we obtain phenol.

*Formanilid*:  $\text{NHBd} + \text{FoO}_2$ , is obtained, simultaneously with oxanilid, when oxalate of anilin is subjected slowly to a temperature of  $160^\circ$  to  $180^\circ$ . There remains a clear fluid residue, which stiffens to a soft crystalline mass. Alcohol dissolves out the formanilid, whilst the oxanilid remains undissolved. From the alcoholic solution it crystallizes in prisms resembling urea.

<i>Succinanilid</i>	. . .	$2(\text{NHBd}) + \text{SuO}_4$ , and
<i>Succinalid</i>	. . .	$\text{NBd} + \text{SuO}_4$ ,
<i>Suberanilid</i>	. . .	$2(\text{NHBd}) + \text{SbO}_4$ , and
<i>Suberanilic Acid</i>	. .	$\text{NH}_2\text{Bd} + \text{SbO}_6$ ,
<i>Camphoranilid</i>	. . .	$2(\text{NHBd}) + \text{CphO}_4$ , and
<i>Camphoranilic Acid</i>	. .	$\text{NH}_2\text{Bd} + \text{CphO}_6$ ,
<i>Phtalanilid</i>	. . .	$2(\text{NHBd}) + \text{PhtO}_4$ , and
<i>Phtalanilic Acid</i>	. .	$\text{NH}_2\text{Bd} + \text{PhtO}_6$ .

<i>Benzanilid</i> ,	$\text{NIIBd} + \text{BzO}_2$ ,	} are formed when the bi- oxychloride of benzoyl, cinnamyl, and of cumi- nyl act with hydrochlo- ric acid upon anilin.
<i>Cinnanilid</i> ,	$\text{NHBd} + (\text{C}_4\text{H}_2) \text{BzO}_2$ ,	
<i>Cuminanilid</i> ,	$\text{NHBd} + \text{CuO}_2$ .	

*Oxanilid* . .  $\text{NHBd} + \text{OxO}_2$ , and  
*Oxanilic Acid*,  $(\text{NHBd}, \text{OxO}_2) \text{OxO}_3$ .  
*Oxanilamid*, see under *Cyananilin*.

*Carbanilid*:  $\text{NHBd} + \text{CO}$ . If we heat anilin-urea (carbanilid-carbamid) it separates into carbanilid and carbamid. We obtain these bodies, most simply, by the action of phosgen gas,  $\text{COCl}_2$ , upon anilin. Carbanilid crystallizes from the hot alcoholic solution in needles of silky lustre; odorless, but, by being heated, it has a suffocating smell, resembling benzoic acid; fuses at  $205^\circ$ ; is volatile. By heating with potash lye, it separates into anilin and carbonic acid.

*Sulpho-carbanilid*:  $\text{NHBd} + \text{CS}$ . If we mix sulpho-carbonic acid with anilin, after a few hours hydrosulphuric acid escapes, whilst the fluid stiffens to a scaly crystalline mass of sulphcarbanilid. It is also obtained when sulphocynate of anilin is heated with evolution of hydrosulphuric acid and sulphide of ammonium. In water, slightly—in alcohol and ether, easily soluble; odor peculiar, melts at  $140^\circ$ , volatile. If we melt it with hydrate of potassa, we obtain anilin and a mixture of carbonate of potassa and sulphide of potassium.

*Sulphanilic Acid*:  $(\text{NH}_2\text{Bd}, \text{SO}_3) \cdot \text{SO}_3$ . If we treat the analids with concentrated sulphuric acid in the heat, we obtain sulphanilic acid and the original acid. If we use oxanilid, carbonic acid and carbonic oxide escape together. Sulphanilic acid crystallizes in large rhombic shining leaflets, which do not dissolve easily in water or alcohol. If we heat the acid with soda-lime, we obtain anilin and sulphuric acid salts. This paired acid saturates 1 atom base.

The substance formerly described as anthranilic acid is probably *carbanilic acid*.

*Chlorcyananilid* arises by the action of parachlorocyanogen upon anilin.

*Oxaluranilid*:  $\text{NH}_2\text{Bd} + \text{N}_2\text{C}_6\text{H}_2\text{O}_6$ , arises by the action of parabanic acid upon anilin.

By the action of bromide of methyl, of ethyl, and of amyl, upon anilin, we obtain bases which, in reality, agree with anilin, and correspond to the formulæ  $\text{NHBdMe}$ ,  $\text{NHBdAe}$ ,  $\text{NBdMe}_2$ , etc. In like manner we obtain, by the varied action of the bromine compounds, bases which consist of nitrogen, benzid, methyl, or ethyl, etc.  $= \text{NBdMeAe}$ ,  $\text{NBdMeAm}$ , etc.

*Cyananilin* (Cyanide of Anilin):  $\text{NH}_2\text{Bd}, \text{Cy}$ . If we lead cyanogen gas into an alcoholic solution of anilin, white odorless spangles are separated, which consist of 1 atom anilin + 1 atom cyanogen, are insoluble in water, with difficulty soluble in alcohol and ether, and will not volatilize undecomposed. Cyananilin possesses the properties of a base, and forms salts which no longer show the reactions of anilin. If we treat it a longer time with dilute acids, it separates into different products. If the solution in dilute hydrochloric acid be evapo-

rated, the dry residue consists of chloride of ammonium and hydrochlorate of anilin, which dissolve in water, and of oxanilid, oxamid, and *oxanilamid* :  $\text{NHBd}, \text{OxO}_2 + \text{NH}_3, \text{OxO}_2$ , *Oxanilamid*, which are separated by hot water. From the hot alcoholic solution, the oxanilamid crystallizes in white silky-lustred flakes, and, with concentrated sulphuric acid, gives sulphanic acid, sulphate of ammonia, carbonic acid, and carbonic oxide.

*Melanilin* :  $(\text{NHBd}, \text{Cy}) \text{NH}_2 \text{Bd}$ . If chloride of cyanogen gas be led into anilin until the latter, by heating, will absorb no more, we thus obtain a solid, black, transparent mass, mainly consisting of hydrochlorate of melanin. Two atoms anilin and 2 atoms chlor-cyanogen, give, by transposition, 1 atom hydrochlorate of melanin. Melanin exhibits a paired base, consisting of cyanilid, as a pairling combined with anilin. We obtain the pure base when the mass is dissolved in hot water, and the base precipitated by potassa, or ammonia. Crystallizes from the alcoholic solution in white, hard, triturable leaflets, which, in the damp air, become red; odorless, of bitter taste, fuses at  $120^\circ$ , and decomposes at  $150^\circ$ , under separation of pure anilin, whilst an amorphous mass remains behind, consisting of  $\text{N}_7\text{C}_{54}\text{H}_{25}$ . Melanin, also, does not show the reactions of anilin. With most of the acids, it gives good crystallizable salts. The amorphous substance may be viewed as a paired compound of anilid-mellan, with anilin :  $\text{N}_7\text{C}_{54}\text{H}_{25} = (\text{NHBd}, \text{N}_4\text{C}_6) + 3(\text{NH}_2\text{Bd})$ .

*Bicyanomelanilin* :  $(\text{NHBd}, 3\text{Cy}) \text{NH}_2 \text{Bd}$ . Melanilin receives 2 atoms more of cyanogen, forming a weak base, which separates, very easily, into ammonia and melanoximid :  $\text{N}_3\text{C}_{30}\text{H}_{11}\text{O}_4$ . If we treat the alcoholic solution of this body with potassa, we obtain oxalic acid and melanilin : it may be considered as double oxalate of melanilin—4 atoms HO. If we subject melanoximid to dry distillation, we obtain *anilocyanic acid* :  $\text{NC}_{14}\text{H}_5\text{O}_2 = \text{HO}(\text{NC}_{14}\text{H}_4)\text{O}$ , with evolution of carbonic oxide and carbonic acid, and formation of carbanilid. Anilocyanic acid is fluid, colorless, easily changed, heavier than water, odor intense, boils at  $180^\circ$ . Anilocyanic acid, in its decompositions, agrees with cyanic acid; by being treated with acids and alkalis it separates into anilin and carbonic acid; in contact with water, into carbanilid and carbonic acid; and in contact with ammonia, into anilin-urea.

*Nitranelin* :  $\text{NH}_2, \text{C}_{12}\text{H}_4(\text{NO}_2) = \text{NH}_2\text{Bd} + \text{NH}_2$  *Nitranelin*.  $(\text{C}_{12}\text{H}_3)_2\text{NO}_4$ . We obtain this base from binitrobenzid, as anilin from nitrobenzid; it crystallizes from the hot solution in yellow needles an inch in length, slightly soluble in cold water, more easily in alcohol and ether, melts at  $110^\circ$ , sublimable, a weak base, all the salts react sour, and color the skin intensely yellow.



*Chloranilin*.  $\text{NH}_2\text{-(C}_{12}\text{H}_4\text{Cl)=NH}_2\text{Bd} + \text{NH}_2\text{(C}_{12}\text{H}_3\text{)Cl}_2$ , distils over when chlorisatin (*see* Indigo) is heated with hydrate of lime; we obtain an oily fluid which stiffens in the receiver. From the hot alcoholic solution it crystallizes in regular octohedrons; in water it is not easily soluble, easily so in alcohol and ether. Tastes and smells like anilin; fuses at  $65^\circ$ , and boils at  $200^\circ$ ; shows the same reactions as anilin; an extremely weak base.

*Bichloranilin*.  $\text{NH}_2\text{-(C}_{12}\text{H}_3\text{)Cl}_2$ , arises by heating bichlorisatin with potassa; not, as yet, better known.

*Trichloranilin*.  $\text{NH}_2\text{-(C}_{12}\text{H}_2\text{Cl)Cl}_2$ , is obtained by the action of chlorine upon chloranilin. Crystallizes in long needles, no longer basic.

*Bromanilin*, *Bibromanilin*, and *Tribromanilin*, correspond to the chlorine compounds, and are similarly obtained.

*Iodanilin*.  $\text{NH}_2\text{-(C}_{12}\text{H}_4\text{I)=NH}_2\text{Bd} + \text{NH}_2\text{-(C}_{12}\text{H}_3\text{)I}_2$ . If we dissolve anilin in anhydrous iodine, after a short time the whole stiffens to a crystalline mass of hydriodate of iodanilin. Ammonia precipitates the base. From the alcoholic solution dazzling white crystals form. The chlorine compounds crystallize in beautiful plates of mother-of-pearl lustre.

*Naphthalidin*.  $\text{NH}_2\text{-(C}_8\text{H}_2\text{-(Bd)=NC}_{20}\text{H}_9$ , is obtained in the same manner from nitronaphthalid, as anilin from nitrobenzid. Crystallizes in silky-lustred, fine, white, flat needles, pressed together; fuses at  $50^\circ$ , boils at  $300^\circ$ ; volatile; possesses a peculiar, strong, unpleasant smell, and strong, bitter, caustic taste; insoluble in water, but easily soluble in alcohol and ether. *Naphthalidin-carbamid*:  $\text{NH}_2\text{-(C}_8\text{H}_2\text{-(Bd)+CO=NH-(C}_8\text{H}_2\text{-(Bd))+CO}$ , is obtained when oxalate of naphthalidin is distilled. If we let sulpho-carbonic acid act upon a solution of naphthalidin, we obtain a compound which must consist of  $\text{C}_{21}\text{H}_8\text{NS}$ . *Seminaphthalidin*:  $\text{NH}_2\text{-(C}_{10}\text{H}_3$ , is obtained by the action of sulphide of hydrogen upon binitronaphthalid. It forms metallic-lustred crystals, changing from yellow into copper-red, which easily dissolve, with a dark color, in alcohol and ether.

*Toluidin*.  $\text{NH}_2\text{,Td=NH}_2\text{,C}_{14}\text{H}_7$ , is obtained from nitrotolid. Crystallizes from the hot, saturated, alcoholic solution, in broad, large leaves, fuses at  $40^\circ$ , boils at  $198^\circ$ , but evaporates even at ordinary temperature. Heavier than water, in which it is only slightly soluble, but easily dissolves in alcohol, ether, wood-spirit, etc.; possesses a burning taste, and odor like wine, aromatic; reacts feebly alkaline, and does not act upon a solution of chloride of lime. Toluidin precipitates oxide of iron from chloride of iron, and gives, with sulphate of copper, a green crystalline precipitate; with chloride of platinum, an orange-colored one, and with nitrate

of silver, a white crystalline. The salts crystallize. If we let bromine act upon *toluidin*, we obtain, probably, *tribrom-toluidin*  $=\text{NH}_2\text{C}_6\text{H}_3\text{Br}_3$ . Towards cyanogen it behaves like anilin, forms cyan-toluidin, and, if we let *chloride of cyanogen* act upon *toluidin*, we obtain a base corresponding to melanilin, called *metatoluidin*, consisting of  $\text{N}_3\text{C}_6\text{H}_7=(\text{NH}_2\text{TdCy})\text{NH}_2\text{Td}$ .

*Xylidin*:  $\text{NH}_2\text{Xd}=\text{NH}_2\text{C}_6\text{H}_9$ . A base, as yet, *Xylidin*. not more intimately known; is obtained by the action of sulphide of hydrogen upon nitroxylid.

*Cumidin*:  $\text{NH}_2\text{Cd}=\text{NH}_2\text{C}_8\text{H}_{11}$ , is obtained from *Cumidin*. nitrocumid. A pale yellow oil, which strongly refracts the light, and, in the cold, stiffens, forming quadrangular plates. Tastes burning, not easily soluble in water, but easily in alcohol and ether, sp. gr. 0.9526; boils at  $225^\circ$ , precipitates salts of peroxide of iron. The salts are mostly colorless, easily crystallizable, dissolve readily in alcohol and ether; reacts acid. With bromine it gives, probably, *tribromcumidin*, and, with cyanogen, *cyancumidin*, corresponding to cyan-anilin. *Nitro-cumidin* arises from binitrocumid in the same way as nitranilin from binitrobenzid. Crystallizes in yellow scales; a weak base, which, however, fully neutralizes acids. If upon nitrocumidin we let *bioxychloride of benzoyl* act, we obtain a substance crystallizing in needles  $=(\text{NH}_2\text{C}_8\text{H}_9\text{NO}_4)+\text{BzO}_2$ . *Chloreinnamyl* and *chlorcuminy* give corresponding compounds.

*Nitromesidin*:  $\text{NH}_2(\text{C}_8\text{H}_{10}\text{NO}_4)$ , is obtained by *Nitromesidin*. the action of sulphide of hydrogen upon binitromesitol. Long gold-colored needles, melts below  $100^\circ$ , volatile. Easily soluble in alcohol and ether, tastes bitter, and does not react acid. The hydrochloric acid salt crystallizes in colorless needles. Also, from trinitromesitol, a basic body is said to be obtained.

*Paranicin*:  $\text{NH}_2\text{C}_{20}\text{H}_{11}$ , arises by the action of *Paranicin*. ammonia upon *nitroparanicin* (page 193). The hydrochloric acid salt crystallizes in octahedrons.

*Cymidin*:  $\text{NH}_2\text{C}_{20}\text{H}_{13}$ . A base not better known, *Cymidin*. which arises from  $\text{C}_{20}\text{H}_{14}$ .

*Chinolin* (Leukol):  $\text{NC}_8\text{H}_8=\text{NH}_2\text{C}_{18}\text{H}_6$ . This *Chinolin*. base is found in coal-tar oil, by the fractional distillation of which it is obtained (*see Anilin*). At  $239^\circ$  chinolin goes over. It is formed farther when cinchonine, quinine, or strychnine is heated with hydrate of lime, whilst hydrogen gas is evolved—as residue carbonate of potassa remains. Chinolin is a colorless oil, of peculiar smell, resembling oil of bitter almonds, and sharp, burning, bitter taste, fluid still at  $-20^\circ$ , boils at  $239^\circ$ ; sp. gr. 1.081; slightly soluble in water. One atom chinolin, at  $0^\circ$ , absorbs 3 atoms water, which at  $100^\circ$ , under turbidity, completely evaporates. It mixes in all proportions with alcohol,

ether, wood-spirit, etc. ; does not coagulate albumen, neither does it react upon chloride of lime. With chromic acid, chinolin gives a yellow precipitate. By permanganate of potassa, it is separated into ammonia and oxalic acid. With acids, it gives crystallizable, strongly bitter salts. Nitrate of peroxide of iron, sulphate of copper, and acetate of lead are not precipitated by chinolin. With nitrate of silver, corrosive sublimate, chloride of gold, platinum and of antimony, and protochloride of tin, it causes white and yellow precipitates. Tannin gives a brown precipitate.

Coniin. *Coniin* (Conia):  $\text{NC}_{16}\text{H}_{15}=\text{N} \begin{cases} \text{H} \\ 2\text{C}_8\text{H}_7 = \text{NHBu}_2 \end{cases}$

According to this last formula, coniin corresponds to ammonia, in which  $\text{H}_2$  is replaced by 2 atoms butyryl, and if we treat coniin with oxidizing bodies, we obtain, in fact, butyric acid. This base is found in all parts of the *Conium maculatum*. It is most easily obtained from the seed, which is crushed, and then distilled with potash lye so long as the distillate gives an acid reaction. The distillate, saturated with dilute sulphuric acid, and evaporated by gentle heat, to syrup thickness, is treated with alcohol containing ether, in which the sulphate of coniin is dissolved. The alcoholic solution is evaporated, afterwards the residue is distilled with potash lye, and the obtained coniin freed from water by chloride of calcium. A colorless, oily fluid; tastes very sharp and offensive; like tobacco, extremely poisonous; odor very penetrating, resembling hemlock; excites tears. Sp. gr. 0.89; boiling point  $170^\circ$  (?). Dissolves more easily in cold water than in warm, and, at a low temperature, absorbs 25 per cent. water. This solution becomes turbid in the warm hand; reacts alkaline. Easily soluble in alcohol, ether, etc. Coniin dissolves sulphur and phosphorus. In the air, it changes to a brown, resin-like mass. Chlorine quickly decomposes it, forming a crystalline volatile substance, soluble in water, alcohol, and ether. Bromine and iodine, also, cause decomposition. Coniin is a strong base, and precipitates many metal oxides from their salts. Oxide and chloride of silver are easily dissolved in it. The salts of coniin are mostly deliquescent, and not easily crystallized. The double salt of platinum crystallizes in four-sided prisms. With corrosive sublimate, it also gives an easily decomposed compound.

Nicotin. *Nicotin*:  $\text{N}_2\text{C}_{20}\text{H}_{14}=\text{NH}_2, (\text{NC}_{20}\text{H}_{12}) = 4$  volumes gas. Nicotin occurs in the genus *Nicotiana* in the vegetable as well as in the seed. Tobacco-smoke contains a considerable quantity of nicotin. It is obtained when the leaves of tobacco are extracted with dilute sulphuric acid, the fluid (somewhat evaporated) distilled with lime, and the distillate shaken with ether, in which nicotin dissolves. After evaporating the etheric solution, the nicotin remains, and is freed from alcohol and water by being heated a long time, and finally distilled in a current of hydrogen gas. A colorless, transparent, oily liquid;



odor strongly tobacco-like, and sharp, burning, long-continued taste; boils at  $180^{\circ}$  (?); volatilizes even at common temperature. Mixes with water(?), alcohol, and ether in all proportions; very poisonous. A strong base, and neutralizes acids completely. Most of the salts are soluble in water; a part crystallize. Inodorous, and taste like tobacco. The aqueous solution of nicotine gives, with chloride of platinum, a yellowish-white, and with corrosive sublimate a white precipitate. The double compound of platinum consists of 1 atom chlornicotine plus 2 atoms of chloride of platinum.

#### PAIRED NITROGEN BASES.

##### *a. Bases artificially produced.*

*Cyanæthin*:  $(N_2C_{18}H_{12})^{\wedge}NH_3$ . If upon nitro-propionyl (cyanethyl), we let potassium act, there *Cyanæthin*. remains a brittle, yellowish residue. From this the cyanide of potassium is extracted by cold water, whilst the cyanæthin remains. From the hot aqueous solution, the cyanæthin crystallizes in white, inodorous, almost tasteless leaflets of mother-of-pearl lustre; melts at  $190^{\circ}$ ; boils at  $280^{\circ}$ , and volatilizes with partial decomposition; reacts feebly alkaline, and gives, with acids, salts easily soluble in water and alcohol; crystallizable, and of bitter astringent taste; from these salts carbonic acid and caustic alkalis separate the base unchanged. The *nitric acid salt*,  $(N_2C_{18}H_{12})^{\wedge}NH_4O + NO_5$ , is neutral, and crystallizes in long, colorless prisms. The base is scarcely decomposed by being heated even with hydrate of lime.

*Lophin*:  $N_2C_{46}H_{16} = (NC_{46}H_{13})^{\wedge}NH_3$ , is formed *Lophin*. when nitro-picramyl (page 227) is subjected to dry distillation, until ammonia is no longer evolved. After cooling, a crystalline residue is found in the retort, which is first extracted with ether, and then treated with boiling alcohol. After cooling, lophin is separated from the alcoholic solution in colorless, silky, penniform prisms; inodorous and tasteless; insoluble in water, not easily soluble in boiling alcohol, ether, and turpentine oil. Volatile; fuses at  $200^{\circ}$ , and stiffens, forming needles. Easily soluble in an alcoholic solution of potassa. A very permanent base. With most of the acids it gives crystallizable combinations, soluble in alcohol, but not in water.

*Amarin* (Benzolin):  $N_2C_{42}H_{18} = (NC_{42}H_{15})^{\wedge}NH_3$ , *Amarin*. is obtained when nitro-picramyl is boiled a few hours with potash lye; amarin separates like resin; it is dissolved in dilute acid and alcohol, and precipitated from the solution by ammonia. From the hot alcoholic solution it crystallizes in six-sided needles, destitute of color, taste, and smell; insoluble in water, soluble in alcohol and ether; fuses at  $100^{\circ}$ , and is decomposed by distillation,



evolving ammonia. If amarin be heated with a mixture of chromate of potassa, sulphuric acid, and water, a large quantity of benzoic acid escapes. Nitric acid causes the same decomposition. The alcoholic solution does not react alkaline. Most of the salts are not easily soluble. The salts of sulphuric, nitric, and hydrochloric acid crystallize.

Furfurin.

*Furfurin*:  $\text{N}_2\text{C}_{30}\text{H}_{12}\text{O}_6 = (\text{NC}_{30}\text{H}_9\text{O}_6)^-\text{NH}_3$ , is obtained when nitro-furfurol is boiled a long time with potash lye. From the boiling aqueous solution it crystallizes in inodorous, fine, white, silky needles, tasting slightly bitter; fuses at  $100^\circ$  to a colorless oily liquid, which a long time after cooling stiffens crystalline. It dissolves in 135 parts boiling water, it is almost insoluble in cold water, but easily soluble in alcohol and ether. A strong base; reacts alkaline, and neutralizes completely the acids. Alkalies and ammonia separate it from its compounds, but if it be boiled with a solution of chloride of ammonium, ammonia escapes. No salt of this base gives precipitates with the solutions of the salts of iron, copper, silver, lime, and baryta, but, probably, with bichloride of mercury and chloride of platinum. The salts crystallize, and are not precipitated by nutgall tincture.

Urea.

*Urea* (Urenoxyd-ammonia):  $(\text{NC}_2\text{H}_3\text{O}_2)^-\text{NH}_3$ . This is the principal constituent of the urine of the mammalia, and contains more nitrogen than any other secretion of that class. It is formed by the transposition of the cyanate of ammonia; it is farther formed by the decomposition of uric acid of alloxan, alloxantin, etc. We obtain urea from urine, when the latter is evaporated by gentle heat to syrup-thickness, the residue mixed with moderately concentrated pure nitric acid, and the mixture, surrounded by ice, left to stand twenty-four hours. During that time yellow, scaly leaflets of nitrate of urea are separated. These are dissolved in warm water and bleached with animal charcoal. To the filtered solution of nitrate of urea carbonate of potassa is added so long as effervescence follows, and then the whole is evaporated upon the water-bath. The residue is treated with alcohol, in which the urea dissolves. If we conduct the vapor of hydrate of cyanic acid into aqueous ammonia, there remains, after evaporating the solution, pure urea. It crystallizes from the alcoholic solution in long, completely white prisms; inodorous; tastes like nitrate of potassa; easily soluble in alcohol and water, insoluble in ether. The solution does not react alkaline. By raising the heat slowly, urea separates first into ammonia, water, and mellanuric acid; when more strongly heated cyanurenic acid remains, which is finally transposed into hydrate of cyanic acid, and is again united with the ammonia, which has gone over, to form urea. If urea be warmed with dilute acids and alkalies, it separates into carbonic acid and ammonia,  $\text{N}_2\text{C}_2\text{H}_4\text{O}_2 \quad \text{HO} =$

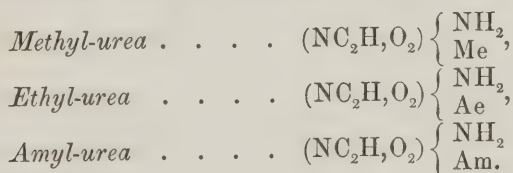
$2\text{NH}_3 + 2\text{CO}_2$  (quantitative determination of urea). If hyponitric acid,  $\text{NO}_2$ , act upon urea, we obtain nitrate of ammonia, together with evolution of equal quantities of carbonic acid and nitrogen gas. Urea is only a weak base.

*Nitrate of Urea:*  $(\text{NC}_2\text{H}_4\text{O}_2)^- \text{NH}_4\text{O} + \text{NO}_3$ , is obtained directly; crystallizes from the aqueous solution in perfectly white leaflets, which dissolve in 8 parts cold water. By heating, it is decomposed, evolving carbonic acid and nitrogen gas.

*Oxalate of Urea:*  $(\text{NC}_2\text{H}_4\text{O}_2)^- \text{NH}_4\text{O} + \text{OxO}_3$ , separates in thin, crystalline leaflets, which taste sour, when to a solution of urea a solution of oxalic acid is added.

Urea, farther, has the property of forming crystallizable compounds with several salts, and in these compounds it seems to play the part of water of crystallization; thus with chloride of ammonium, chloride of sodium and of mercury, etc. The combination with *common salt*  $= \text{NaCl} + (\text{NC}_2\text{H}_4\text{O}_2)^- \text{NH}_3 + 2\text{aq}$ , crystallizes in shining, rhombic prisms.

If we conduct ammonia gas into the cyanate of methyl, of ethyl, or amyl, we obtain compounds of urea with  $\text{C}_2\text{H}_5$ ,  $2\text{C}_2\text{H}_5$ , and  $5\text{C}_2\text{H}_5$  (page 325). But these compounds may also be considered as paired compounds of methyl-amin, ethyl-amin, and amyl-amin with oxide of urea. Then the formulæ for these compounds are:—



(Compare page 325).

*Anilin-urea* (Carbamid, Carbanilid):  $(\text{NC}_2\text{H}_4\text{O}_2) \left\{ \begin{array}{l} \text{NH}_2 \\ \text{C}_{12}\text{H}_5 \end{array} \right. = (\text{NC}_2\text{H}_4\text{O}_2)\text{NH}_2\text{Bd}$ , is obtained when vapor of hydrate of cyanic acid is conducted slowly and at a low temperature to anilin. It is also, obtained when chloride of cyanogen gas acts upon aqueous anilin; also, by mixing sulphate of anilin with a solution of cyanate of potassa. Crystallizes in needles; separates by being heated into carbamid and carbanilid; if the temperature be raised ammonia escapes, and then the crystalline residue consists of carbanilid and cyanuric acid. If we let chloride of cyanogen act upon *nitrilanin*, we obtain *binitro-melanilin* and *nitrilanin-urea*,  $(\text{NC}_2\text{H}_4\text{O}_2) \left\{ \begin{array}{l} \text{NH}_2 \\ \text{C}_{12}\text{H}_4(\text{NO}_2)_2 \end{array} \right.$ , which crystallizes in long, yellow needles; both compounds are destitute of acid properties.

*Guanin:*  $\text{N}_5\text{C}_{10}\text{H}_5\text{O}_2$ , occurs in small quantity in guano. We digest guano with dilute lime-water,

until, by boiling, the fluid appears greenish yellow; filter, and saturate with hydrochloric acid. After a few hours, a precipitate is formed consisting of guanin and uric acid; we boil this with hydrochloric acid, and precipitate the guanin from the hydrochloric acid solution by ammonia. A white substance, in the form of a powder, bears a high temperature without decomposing. With acids it gives salt-like compounds, which, however, are very easily decomposed, even by warming. Guanin dissolves more easily in pure potassa and soda than in acids, and forms with soda a crystallizable compound; the combinations with lime and baryta are at once decomposed by carbonic acid.

Melam.

*Melam*:  $N_{11}C_{12}H_9$ . If 2 parts chloride of ammonium and 1 part sulphocyanide of potassium, be subjected to slow distillation until no more products of decomposition escape, then the residue contains melam, chloride of potassium, and chloride of ammonium; the first of which remains when the mass is treated with water. A white, completely indifferent body; insoluble in water, alcohol, and ether. Fused with hydrate of potassa, ammonia and cyanate of potassa are formed.

Melamin.

*Melamin*:  $N_6C_6H_6 = (NH_3, N_4C_6)^-NH_3$ . If we boil melam with moderately concentrated potassa solution until it completely disappears, and then evaporate the solution to a certain concentration, leaflets of melamin are separated, and the solution contains ammelin in combination with potassa. One atom melam plus 2 atoms water are equal to 1 atom melamin and 1 atom ammelin,  $N_5C_6H_5O_2$ ; 1 atom melam plus 1 atom ammonia are equal to 2 atoms melamin; thus, therefore, 1 atom melam withdraws 1 atom of ammonia from the second atom melam and is changed into melamin; in the place of ammonia 4 atoms HO enter, and form 2 atoms ammelin. From the boiling aqueous solution melamin crystallizes in colorless, bright, lusted, rhombic octohedrons. Insoluble in alcohol and ether, not easily in cold water. In a high temperature it decomposes into melan (?), evolving ammonia. It combines like urea with acids and salts.

Ammelin.

*Ammelin*:  $N_5C_6H_5O_2 = (2HON_4C_6)^-NH_3$ . If to the alkaline solution of ammelin (*see* Melamin) we add acetic acid, or a solution of chloride of ammonia, ammelin is precipitated. This body is also formed by the action of dilute acids upon melam and melamin. From the solution of pure nitrates, ammonia precipitates ammelin pure. It appears as a dazzling white, crystalline powder; insoluble in water, alcohol, and ether; easily soluble in pure alkalies and in most of the acids. It decomposes in a high temperature; fused with hydrate of potassa, it gives cyanate of potassa and ammonia. A weak base; with most of the acids, it gives crystallizable salts, which, even by being overflowed with water, are partially decomposed, forming acid compounds. It also combines, like urea, with salts. The nitrate appears in large colorless crystals.



*Ammelid*:  $2\text{HIO} + (4\text{HIO}, 2\text{N}_4\text{C}_6)\text{NH}_3$ , is formed Ammelid.  
in a solution of melam in warmed nitric acid of 1.49 sp. gr.; farther, by the action of concentrated sulphuric acid upon ammelin and melam, as also by the decomposition of ammelin and melamin with dilute nitric acid. If we add alcohol to a solution of ammelin in concentrated sulphuric acid, ammelid is separated. After being washed with water, it resembles ammelin, but it no longer possesses basic properties. If we boil ammelid with nitric acid, we obtain cyanurenic acid and ammonia, and fused with hydrate of potassa, it separates into cyanic acid and ammonia. With oxide of silver it gives a compound consisting of  $2\text{AgO} + (4\text{HIO}, 2\text{N}_4\text{C}_6)\text{NH}$ .

*Caffein* (Thein, Guaranin):  $\text{N}_4\text{C}_{16}\text{H}_{10}\text{O}_4 = (2\text{CH}_2,$

$\text{N}_2\text{C}_8\text{O}_4)\text{N} \begin{cases} \text{H}_2, \text{HCy.} \\ \text{Me} \end{cases}$  Caffein. Caffein appears as a paired

compound of hydrocyanate of methylamin with uric acid, in which uren-imid is substituted by  $2\text{C}_2\text{H}_2$ . It occurs in coffee kernels, in tea, in the fruit of *Paullinia sorbilis*, and in the leaves of *Ilex paraguayensis*. Crude coffee is boiled with water, the obtained decoction first precipitated with a solution of sugar of lead, and then boiled with the hydrate of oxide of lead until a new quantity is not colored. From the filtered solution caffein is procured by evaporation. Crystallizes in flexible, silky needles; fuses at  $177^\circ$ , and sublimes at  $384^\circ$ . The crystals grate between the teeth, and have a sharp, bitter taste. Caffein dissolves in 98 parts cold water, in 97 parts alcohol, and 194 parts ether. It is absorbed in large quantity by boiling water. It possesses but weak basic properties. The *hydrochlorate of caffein* is separated in beautiful crystals, if caffein be dissolved in concentrated hydrochloric acid; loses the acid even at  $100^\circ$ . Also the sulphate crystallizes, but by being treated with water, it is completely decomposed. Caffein combines farther with chloride of mercury, chloride of gold, etc. If it be boiled with baryta-water, we obtain, at first, carbonate of baryta, and in the solution, it is said, cyanate of baryta is found. *Chlor-caffein*,  $\text{N}_4\text{C}_{16}\text{H}_9\text{ClO}_4$ , is formed simultaneously with amelinic acid, cholestrophan, and methylamin, by the decomposition of caffein by chlorine. (Compare p. 334).

*Theobromin*:  $\text{N}_4\text{C}_{14}\text{H}_8\text{O}_4 = (\text{C}_2\text{H}_2, \text{N}_2\text{C}_8\text{O}_4)\text{NH}_2\text{Me}, \text{HCy}$ . This substance is obtained from cacaonuts in the same Theobromin.  
manner as caffein from coffee. It appears in the form of a white crystalline powder of feebly bitter taste; little soluble in water, alcohol, and ether. Scarcely possesses basic properties. The *hydrochloric acid compound* is separated in crystals from the concentrated hydrochloric acid solution. The *nitric acid salt* crystallizes in rhombic columns. Theobromin gives, with nitrate of silver, a crystallizable compound,  $\text{N}_4\text{C}_{14}\text{H}_8\text{O}_4 + \text{AgO}, \text{NO}_3$ . Theobromin contains  $\text{C}_2\text{H}_2$  less than caffein.



*Creatinin*:  $\text{N}_3\text{C}_8\text{H}_7\text{O}_2 = (\text{N}_2\text{C}_8\text{H}_4\text{O}_2)\text{NH}_3$ . This base is found in human urine, and in muscle, and is formed by the action of acids upon creatin. We boil putrid human urine with lime-water so long as ammonia is evolved, evaporate the filtrate, leave the salts of urine to crystallize, then add chloride of zinc thereto, by which, after a long time, crystals of creatinin, with chloride of zinc, are formed, which crystals are purified by repeated crystallization. These crystals are dissolved in boiling water; the solution is mixed with ammonia until it begins to be turbid, then it is precipitated by sulphide of ammonium, filtered, the filtrate evaporated, and the residue dissolved in alcohol. From the alcoholic solution, the creatinin, after long standing, crystallizes. Or we evaporate the solution of 1 part creatin in 1 part sulphuric acid and 3 parts water, decompose the sulphate of creatinin by boiling with carbonate of baryta, filter, and leave to crystallize. It appears in colorless, oblique, rhombic columns, tastes caustic, dissolves in 11.5 parts water and in 102 parts absolute alcohol. The *sulphate of creatinin* crystallizes in water-clear quadratic plates, and the hydrochlorate in transparent acid-reacting leaflets. The combination, with chloride of zinc, appears in oblique rhombic columns, which are not easily soluble in water, and are insoluble in alcohol and ether.

*Thiosinnamin*:  $(\text{NC}_8\text{H}_5\text{S}_2)\text{NH}_3$ . If we shake 1 part oil of mustard with 3 to 4 fold volumes of strong aqueous ammonia, the whole, after a short time, stiffens to a crystalline mass of thiosinnamin. It appears in shining white crystals, inodorous, bitter; fuses at  $70^\circ$ , dissolves easily in water, does not react alkaline, and is not volatile. Is only a weak base, and with sulphuric, nitric, acetic, and oxalic acid, it gives no fixed compounds. It unites, like urea, with several salts, with chloride of mercury, chloride of silver, sulphate of copper, and nitrate of silver. If to a concentrated solution of thiosinnamin nitrate of silver be added, there is formed a voluminous crystalline precipitate, consisting of  $\text{AgO}, \text{NO}_5 + (\text{NC}_8\text{H}_5\text{S}_2)\text{NH}_3$ , and, by being boiled with water, is decomposed, whilst sulphide of silver is separated.

*Sinnamin*:  $(\text{NC}_8\text{H}_3)\text{NH}_3$ . If we digest thiosinnamin with freshly precipitated hydrate of oxide of lead, mixed with water until it is like pap, and then after the entire decomposition of the mass, we extract it first with water, and then again with alcohol, there remains, after evaporation upon the water-bath, a thick syrup, in which, after long standing, four-sided prisms form, which contain 1 atom more of water. The syrup-like sinnamin contains less water than the crystallized; inodorous, and of strongly bitter taste. It is decomposed by heating, and, by boiling with hydrochloric acid, whilst ammonia is evolved. A strong base, reacts alkaline, precipitates the salts of

oxide of lead, copper, iron, and silver; separates ammonia from its compounds.

*Sinapolin*:  $(\text{NC}_{14}\text{H}_9\text{O}_2)\text{NH}_3$ . If we heat mustard oil with baryta water, and evaporate the whole to dryness, sinapolin remains, and can be extracted by alcohol or ether. It is also obtained by the action of hydrated oxide of lead upon mustard oil. Crystallizes from the aqueous solution in unctuous shining leaflets, which fuse at  $100^\circ$ . In the hot aqueous solution it reacts alkaline. Is not decomposed by boiling with potassa lye. Dissolves in acids.

*Thialdin*:  $(\text{C}_{12}\text{H}_{10}\text{S}_4)\text{NH}_3$ . Into a solution of aldehyd-ammonia in 12 to 16 parts water, we slowly lead hydrosulphuric acid. The crystals which are after a short time deposited, are dissolved in ether, then some alcohol is added, and the solution is left to evaporate spontaneously. The crystals are long, transparent, colorless, shining; the odor, at first, peculiarly aromatic—later, disagreeable. Fuses at  $43^\circ$ , little soluble in water, easily soluble in alcohol and ether. The aqueous solution distillable; heated by itself it decomposes, forming a badly smelling oil. Does not react alkaline. The alcoholic solution gives, with acetate of lead, after a short time, a yellow precipitate, which soon becomes black. If we heat it with a solution of nitrate of silver, aldehyd escapes, whilst sulphide of silver is separated. When heated to redness, with hydrate of potassa, it gives chinolin. If we boil thialdin in a retort with a solution of cyanide of mercury, we obtain sulphide of mercury, and in the neck of the retort appear volatile crystalline needles, which dissolve easily in alcohol and ether, and, probably, contain cyanogen. *Hydrochlorate of thialdin* crystallizes in long prisms, which dissolve easily in water. The *nitric acid salt* exhibits white needles.

*Selenaldin*. If we conduct hydro-selenium into a solution of aldehyd-ammonia, we thus obtain selenaldin, which agrees in its properties with thialdin. A *tellur-aldin* is not known.

*Carbothialdin*:  $(\text{C}_5\text{H}_2\text{S}_2)\text{NH}_3$ . If to an alcoholic solution of aldehyd-ammonia, sulpho-carbonic acid be added, shining white crystals of carbothialdin are separated. Insoluble in water and in cold ether, easily soluble in hot alcohol. By boiling with hydrochloric acid it separates into ammonia, sulpho-carbonic acid, and aldehyd. Dissolves in dilute hydrochloric acid without decomposition; after a little time the solution stiffens to a white pap, insoluble in water. In the hot alcoholic solution, with oxalic acid, it gives oxalate of ammonia.

### b. Organic Vegetable Bases.

Organic vegetable bases.

In plants are found many bases, which behave quite like ammonia, and of which it has been assumed, until now, that they contain ammonia as active part, combined with an organic oxide as pairing. New researches upon quinin (chinin), caffen, piperin, etc., have, however, made it in a high degree probable, that other simple nitrogen bases can take the place of ammonia in the paired bases. There are, however, before us, too few facts to enable us, at present, to exhibit rational formulæ in these respects. On account of this uncertainty, I have preferred to use now the simplest symbol for each of the following bases, and, in order to give the relations to ammonia, in combinations with the acids, to annex the symbol H and H<sub>2</sub>O to the base; e. g.

Morphin . . . . .	Mo,
Hydrochlorate of morphin . .	MoH, Cl,
Sulphate of morphin . . . .	MoH, O + SO <sub>3</sub> .

A few general properties of these bases.

Almost all the bases of this class are solid, crystallizable, and suffer, by dry distillation, a partial or total decomposition. They are almost insoluble in water, but, on the other hand, soluble in alcohol, and many, also, in ether. They possess, alone, as well as in their salts, a bitter, and often most disagreeable taste. Many, as veratrin, strychnin, and brucin, act extremely poisonously upon the animal organism. Their alkaline properties are very different; the stronger, as brucin, strychnin, and quinin, precipitate the oxides of most heavy metals. Many salts are soluble, with difficulty, in water, and can be produced by double decomposition. Many organic bases, which are precipitated by bicarbonate of potassa, remain dissolved, if there be previously added to them tartaric acid, as salts of morphin, brucin, and quinin, whilst the salts of strychnin, narcotin, and cinchonin, are precipitated. With the reagents of organic bases may be enumerated, pure alkalies and their carbonates, phosphate of soda, iodic acid, chloride of gold, of platinum, bichloride of mercury, sulphocyanide of potassium, iodide of potassium, tincture of gall-nuts, and pikrin-nitric acid. If we let the halogens act upon the organic bases, a substitution generally takes place of the hydrogen in the pairing whereby bases arise, containing chlorine, bromine, and iodine.

Production of the bases.

The non-volatile bases are generally produced when the vegetable matter is extracted by acidulated water (sulphuric or hydrochloric acid) and the bases precipitated from the concentrated solution by an alkali (potassa

lime, ammonia, sometimes, also, magnesia). The precipitate is dried, afterwards boiled in alcohol, which dissolves the bases; these are then purified by repeated crystallization, treatment with animal charcoal, etc. They can also be obtained if the acid vegetable extract be exactly saturated with carbonate of potassa, and then an infusion of nutgalls so long added as a precipitate of tannic acid is formed. This precipitate is washed, still moist, mixed with hydrate of lime, and the whole exposed to the air to the destruction of the tannin. Afterward the mixture is dried, and the base dissolved, by boiling alcohol. If several bases occur, in common, they must be separated by different means of solution.

*Aconitin* :  $\text{Ac}=\text{NC}_{60}\text{H}_{47}\text{O}_{14}$ , is found in *Aconitum* Aconitin.  
*napellus*. Crystallizes from the aqueous alcoholic solution in inodorous, bitter, sharp-tasting white grains. Dissolves in 100 parts cold water and 50 parts boiling, easily soluble in alcohol and ether, easily melts, reacts strongly alkaline, and completely saturates acids. The salts are not crystallizable, but appear as a gum-like mass, which tastes sharp and bitter. The pure bases, as well as their salts, are very poisonous.

*Atropin* :  $\text{At}=\text{NC}_{34}\text{H}_{23}\text{O}_6$ . It is found in every Atropin.  
part of *Atropa belladonna*. Crystallizes from the hot concentrated aqueous solution in tuftiform, united, white, transparent prisms of silky lustre. Inodorous, tastes most disagreeably bitter, produces great distention of the pupil, dissolves in 2000 parts cold water, and 54 parts of hot. Easily soluble in alcohol, and in 25 parts cold ether. Even by long boiling with water, atropin suffers a change; it is decomposed by caustic alkalies, under evolution of ammonia and the formation of a resin-like substance. Atropin reacts strongly and permanently alkaline, forms mostly crystallizable, neutral, bitter, and sharp-tasting poisonous salts, which dissolve in water and alcohol, but not in ether.

*Daturin*. It is found in *Datura stramonium*. Daturin.  
Crystallizes from the aqueous alcoholic solution in colorless, very shining, tuftiform needles. Inodorous, and of a bitter taste, strongly resembling that of tobacco. Dissolves in 280 parts cold water and in 72 parts boiling, in 3 parts alcohol and in 21 parts ether; fuses and volatilizes partly undecomposed. Strongly alkaline, and forms neutral, sharp, and bitter-tasting, very poisonous, crystallizable salts soluble in water and alcohol. This compound must be identical with atropin.

*Hyoscyamin* is found in *Hyoscyamus niger* and Hyoscyamin.  
*albus*, particularly in the seed. Crystallizes in needles of silky lustre; smells most offensively, benumbing, tobacco-like; tastes sharply biting; easily soluble in water and alcohol, most poisonous, volatile, and forms neutral salts.



*Bases in Opium.* Opium contains several organic bases as codein, morphin, narcotin, thebain, narcein, and papaverin united to meconic acid and also meconin.

1. Codein. *Codein* (Codeia):  $\text{Co}=\text{NC}_{36}\text{H}_{20}\text{O}_6$ . If we add chloride of calcium to a concentrated aqueous extract of opium, the solution filtered from meconate of lime contains some hydrochlorate of codein and of morphin. Both bases are precipitated by soda, the precipitate treated with alcohol, the alcoholic solution accurately saturated with sulphuric acid, the alcohol evaporated, cold water added to the residue so long as a clouding follows, the solution filtered, and the filtrate evaporated to syrup-thickness. The residue is shaken with potassa solution and ether, which dissolves the codein, and this latter is left behind by spontaneous evaporation of the etheric solution. Crystallizes by slow cooling from the hot saturated aqueous solution, partly in rhombic octohedrons with 2 atoms HO; melts at  $150^\circ$ ; stiffens crystalline; dissolves in 85 parts water at  $15^\circ$ . A strong base which is not expelled by ammonia, gives with acids perfectly neutral bitter-tasting salts; mostly crystallizable. Acts somewhat like morphin.

2. Morphin. *Morphin* (Morphia):  $\text{Mo}=\text{NC}_{36}\text{H}_{20}\text{O}_6$ . The following method for preparing morphin is based upon the property of that substance to form a soluble combination with lime. We extract opium repeatedly with threefold weight of water, boil the fluid, and add by degrees  $\frac{1}{6}$ th as much lime in pap as the amount of opium employed. Afterwards it is strained through linen and the obtained fluid evaporated to double the weight of the opium employed. We filter, heat the filtrate to boiling, and add thereto  $\frac{1}{6}$ th as much chloride of ammonium as the weight of the opium whereby the morphin is precipitated. Forms shining, colorless crystals, which contain 2 atoms water. If morphin be precipitated from its salts by ammonia, we obtain a cheesy precipitate, which after a little time unites crystalline. Inodorous; of strong, bitter taste; almost insoluble in cold water, soluble in 400 parts boiling water, in 13.3 parts hot alcohol, and insoluble in ether; melts in anhydrous condition and stiffens crystalline. *Nitric acid* imparts to morphin and its salts a red color, which soon disappears; treated with *superoxide of lead* and *sulphuric acid*, we obtain a brown, bitter-tasting mass—*morphetin*; easily soluble in water. *Chlorine* and *iodine* produce decomposition. If morphin or its salts be added to a solution of *perchloride of iron*, the solution is colored a beautiful blue. The solution of morphin reacts strongly alkaline; it forms with *acids* neutral, colorless, bitter, sharp-tasting, mostly crystalline salts. *Hydrochlorate of morphin*:  $\text{MoII} + \text{Cl}$ , crystallizes in fine prisms, which dissolve in 20 parts water. *Acetate of morphin*,  $\text{MoII}, \text{O} + \text{AcO}_3$ , is obtained if morphin be diffused in boiling alcohol and enough acetic acid added for complete solution. After cooling, ether is poured over the solution and the salt is

obtained, by standing at rest, in small crystals. More easily soluble in water than in alcohol; the aqueous solution by evaporation loses acetic acid.

*Morphin* is precipitated by ammonia, *codein* is not; the former is insoluble in ether, the latter is soluble. Also morphin and codein differ in their behavior to nitric acid and to perchloride of iron.

*Thebain*,  $\text{NC}_{25}\text{H}_{14}\text{O}_3$ ; *narcein*,  $\text{NC}_{33}\text{H}_{20}\text{O}_{12}$ , and *pseudomorphin*,  $\text{NC}_{54}\text{H}_{13}\text{O}_{14}$ , are bases of opium, which need a more particular investigation.

*Narcotin* (Opian, Narcotina):  $\text{NC}_{46}\text{H}_{25}\text{O}_{14}$ . Nar- 3. Narcotin. cotin is soluble in ether, and can, therefore, if it occur in common with morphin, be separated by that fluid. We obtain it direct when the watery extract of opium is digested with ether. The narcotin remaining behind from the etheric solution is purified by solution in alcohol and recrystallization. Crystallizes in colorless prisms or scales of mother-of-pearl lustre; inodorous, tasteless; fuses at  $170^\circ$  and stiffens at  $130^\circ$ ; insoluble in cold water; 100 parts alcohol of 85 per cent. dissolve, by boiling, 5 parts narcotin, and 100 parts boiling ether dissolve 2.1 parts. If narcotin be dissolved in an excess of sulphuric acid and the solution heated with finely-ground peroxide of manganese, it decomposes into cotarnin and opianic acid (see Opianic Acid) under evolution of carbonic acid.

One atom narcotin,  $\text{NC}_{46}\text{H}_{25}\text{O}_{14} + \text{O}_5 = 1$  atom cotarnin,  $\text{NC}_{26}\text{H}_{12}\text{O}_5 + 1$  atom opianic acid  $\text{C}_{20}\text{H}_8\text{O}_9 + 5\text{HO}$ . The like decomposition follows also, if narcotin be boiled with a large excess of chloride of platinum. If we use but little chloride of platinum, the narcotin decomposes into narcogenin,  $\text{N}_2\text{C}_{72}\text{H}_{38}\text{O}_{20}$ , and into opianic acid. Two atoms narcotin plus 5 atoms oxygen are equal to 1 atom narcogenin, 1 atom opianic acid, and 3 atoms water. Treated with superoxide of lead and dilute sulphuric acid, we obtain narcotein, a brown, amorphous, extremely bitter substance; easily soluble in water and alcohol. If narcotin be heated in an oil-bath a few degrees above fusion, it is colored deep reddish-yellow; at  $220^\circ$  ammonia is evolved under swelling. The swollen residue contains humopinic acid and a new base not yet particularly investigated. If we heat narcotin with a concentrated solution of potassa, it evolves no ammonia, and, if the action be long continued, a body is deposited of the consistence of turpentine—the narcotinate of potassa. Narcotinic acid cannot be isolated, because it is converted again into narcotin. If narcotin be melted with hydrate of potassa at  $220^\circ$ , we obtain propylamin,  $\text{NH}_2\text{C}_6\text{H}_7$  (vide page 359). Narcotin is a weak base. The salts taste more bitter than those of morphin; those with weak acids are decomposed by water under deposition of narcotin.

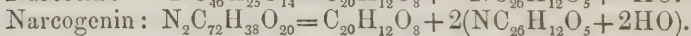
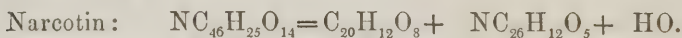
*Difference between Narcotin and Morphin.* Narcotin is taste-

less, soluble in ether, insoluble in pure alkalies, and does not color the salts of peroxide of iron blue. If we add a few drops of nitric acid to a solution of narcotin in sulphuric acid, it assumes, after a few moments, a blood-red color, whilst morphin is colored slightly green. Narcotin, mixed with some alcohol, is precipitated by double carbonate of potassa, but the morphin salts are not. The *narcotin salts* are said to show no medical action. The *morphin salts* act like *opium*.

Products of decomposition of narcotin. Cotarnin. *Cotarnin* (Cotarnia):  $\text{NC}_{26}\text{H}_{12}\text{O}_5 + \text{aq.}$  It is found in the reddish-yellow fluid from which opianic acid has been deposited, by the action of peroxide of manganese upon narcotin, and is precipitated as a double salt by chloride of platinum. The double salt is decomposed by hydrosulphuric acid: we filter from sulphide of platinum, mix the solution of hydrochlorate of cotarnin with baryta water, evaporate, and extract the cotarnin from the residue by alcohol. Crystallizes in stelliform groups of needles, which melt at  $100^\circ$  under loss of 7.5 per cent. of water. Soluble in water, alcohol, ether, and potash lye; dissolves in nitric acid, with dark-red color. The aqueous solution reacts feebly alkaline; it precipitates *salts of peroxide of copper* and of *iron*. The *cotarnin salts* are remarkably soluble, and are obtained direct.

Narcogenin. *Narcogenin*:  $\text{N}_2\text{C}_{72}\text{H}_{38}\text{O}_{20}$ . Only known in combinations of chloride of platinum. If we endeavor to separate it from the platinum compound, it decomposes into narcotin and cotarnin. The chloride of platinum compound crystallizes in light yellow needles.

We can regard narcotin and narcogenin as compounds of cotarnin, with  $\text{C}_{20}\text{H}_{12}\text{O}_8$ , which body then, by oxidation, forms opianic acid.



Humopinic acid. *Humopinic Acid*:  $\text{C}_{48}\text{H}_{23}\text{O}_{17}$ . Humopinic acid, which is formed by heating narcotin, appears as a dark-brown amorphous substance, insoluble in water and acids; dissolves in alcohol, with a deep yellow-red color. *Apophyllenic acid* is occasionally found in the baryta residue, from which cotarnin has been extracted by alcohol.

4. Papaverin. *Papaverin*:  $\text{Pa} = \text{NC}_{40}\text{H}_{21}\text{O}_8$ . To procure papaverin, we use the brown resinous mass, which is obtained, if crude morphin, precipitated by soda from the aqueous extract of opium, be treated with alcohol, the brown extract evaporated, the residue digested with dilute hydrochloric acid, and the filtrate precipitated with ammonia. If we mix the hydrochloric acid solution of this resin with acetate of potassa, a dark resinous body is precipitated, from which, after washing with

water, the papaverin is extracted by boiling ether. Crystallizes from the alcoholic solution in little white spears, scarcely reacting alkaline. The hydrochlorate,  $\text{PaH} + \text{Cl}$ , crystallizes in direct rhombic columns. Not poisonous.

*Chelidonin*:  $\text{Che} = \text{N}_3\text{C}_{40}\text{H}_{20}\text{O}_6$ , is found in all parts of *Chelidonium majus*, in common with chelerythrin. Chelidonin.

Crystallizes from the alcoholic solution, in colorless, inodorous, tabular crystals, insoluble in water, easily soluble in alcohol and ether, melts to a colorless liquid, and, by melting with hydrate of potassa, evolves ammonia. The salts are colorless, mostly soluble in water, react acid; animal charcoal extracts chelidonin from the salts.

*Chelerythrin*:  $\text{Chr} = \text{NC}_{37}\text{H}_{16}\text{O}_8$ , is found in *Chelidonium majus*, particularly in the root, and in the root but not the herb of *Glaucium luteum*, as well as in the root of *Sanguinaria canadensis*. Precipitated from the hydrochloric acid solution by ammonia, it appears in pale-yellow flakes, which, after drying in gentle heat, appear as an adhesive yellow powder; the powder excites violent sneezing and catarrh. It remains from the etheric solution as a turpentine-like mass, which, by degrees, stiffens; from the alcoholic solution it is obtained in warty crystals; the alcoholic solution has a sharp burning taste; melts to an oil-like liquid. If an acid be poured over this base it is colored splendid carmine-red; it completely saturates acids, and forms red salts, of a sharp burning taste, which easily dissolve in water and alcohol, crystallize, and act as narcotics. Chelerythrin.

*Glaucin* is found in the herb of *Glaucium luteum*. Crystallizes from the aqueous solution in small leaflets of mother-of-pearl lustre. If it be precipitated by ammonia from a solution in acids, it appears soft, and dries, after some time, to a hard resinous mass; tastes sharply bitter; soluble in water, alcohol, and ether. Gives, with acids, neutral salts of sharp burning taste. Glaucin.

*Glaucopierin* is found in the root of *Glaucium luteum*. Crystallizes from the etheric solution in dazzling white granular crystals. Easily soluble in water, soluble, with difficulty, in alcohol and ether, tastes exceedingly bitter. By warming with sulphuric acid it assumes a beautiful dark-green color, which soon disappears. Glaucopierin.

*Solanin*:  $\text{So} = \text{NC}_{84}\text{H}_{73}\text{O}_{23}$  (?), is found in the berries of *Solanum nigrum* and *verbasicum*; in the stalks, leaves, and berries of *Solanum dulcamara* and *tuberosum*. Crystallizes from the hot alcoholic solution in microscopic prisms. Colorless; after drying, inodorous; tastes sharply, bitter, aromatic, and produces permanent itching in the esophagus; almost insoluble in water, rather soluble in alcohol, soluble with difficulty in ether. Slightly alkaline; gives, with acids, salts of a bitter, itching taste, which mostly dry away gum-like. The acid salts Solanin.



have a great tendency to form double salts. The succinates crystallize in colorless needles; easily soluble in water. In large doses it acts poisonously.

**Delphinin.** *Delphinin*:  $\text{De}=\text{NC}_{27}\text{H}_{19}\text{O}_7$ , is found in the kernels of the stavesacre (seeds of *Delphinium staphisagria*). Cannot be obtained crystalline; has a pale-yellow resinous appearance; smells slightly like amber; almost insoluble in water, and of insupportable sharp taste; melts at  $120^\circ$ ; forms, with acids, easily soluble salts of extraordinary sharp taste.

**Veratrin.** *Vetratrin* (*Vetraria*):  $\text{Ve}=\text{NC}_{34}\text{H}_{22}\text{O}_6$ , is found in the root of *Veratrum album* and in the seeds of *Veratrum sabadilla*. It appears in the form of a white, uncrystallizable, pulverizable resin; melts at  $110^\circ$ ; reacts strongly alkaline; is inodorous; excites violent sneezing; tastes extremely sharp; insoluble in water, easily soluble in alcohol and ether. It completely saturates bases, and gives, in part, crystallizable salts. Nitric acid colors veratrin first red and then yellow.

**Sabadillin.** *Sabadillin*:  $\text{Sa}=\text{NC}_{20}\text{H}_{13}\text{O}_5$ . It is found in *Veratrum sabadilla*. Crystallizes in stelliform groups of prisms; of insupportable sharp taste; melts at  $200^\circ$ ; soluble in boiling water, insoluble in cold water and ether, easily soluble in alcohol; sublimable; reacts strongly alkaline.

**Jervin.** *Jervin*:  $\text{Je}=\text{N}_2\text{C}_{60}\text{H}_{45}\text{O}_5$ , is found with veratrin in the root of *Veratrum album*; the sulphate of jervin is soluble with difficulty, and the sulphate of veratrin is easily soluble; hence the two salts can be easily separated. It is white, crystalline, fusible; almost insoluble in water, soluble in alcohol; decomposes at  $200^\circ$ .

**Colchicin.** *Colchicin* is found in the seeds of *Colchicum autumnale*. From the solution in alcohol mixed with some water, it crystallizes in colorless prisms and needles. Inodorous; of a sharp, bitter, itching taste; dissolves rather easily in water; slightly alkaline, but completely neutralizes acids, and forms salts in part crystallizable, and of a bitter, itching taste. Nitric acid produces a blue color, which soon disappears.

**Emetin.** *Emetin* (*Emeta*) is found in the root of *Cephaëlis emetica*, *Callicocca*, *pecacuanha*, and *Viola emetica* (*Ipecacuanha*). White, inodorous, almost tasteless powder; unchangeable in the air, and of strong alkaline properties. Easily soluble in alcohol, soluble with difficulty in water, and insoluble in ether. A slight dose produces violent vomiting. Emetin completely saturates acids; the neutral salts appear as a gum-like mass; the acid salts crystallize in part; they mostly dissolve easily in water, act like emetin, and possess a bitter, sharp taste.

**Strychnin.** *Strychnin* (*Strychnia*):  $\text{Str}=\text{N}_2\text{C}_{42}\text{H}_{22}\text{O}_4$ . It is found in several species of the genus *Strychnos*, as in

*Str. nux vomica*, *ignatia*, and *colubrina* in company with *brucin*; also it is found in the poisonous preparation, which the natives of Borneo employ to poison their arrows (*upas-tienté* or *woorara*). Belongs to the most poisonous organic compounds. We procure strychnin most easily from the *Ignatius* beans, which contain very little *brucin*, if these are rasped and completely extracted with ether to remove the fat. The beans, freed from fat, are boiled with alcohol, then the alcohol distilled off, and the residue boiled with water and magnesia. The precipitate is washed, dried, and then treated with anhydrous alcohol, which dissolves the strychnin. From *nux vomica* we obtain strychnin in common with leucin. We separate the bases by converting them into nitrates; the nitrate of strychnin first forms penniform, completely white, small crystals; and later, the nitrate of *brucin*, large, hard, quadrilateral crystals. Also, the separation can be effected by alcohol, which dissolves *brucin* easily and strychnin with difficulty. From the solution in alcohol mixed with some water, strychnin crystallizes, by spontaneous evaporation, in small, white, quadratic prisms; by quick evaporation we obtain it in granular powder; inodorous, and of most bitter, afterwards somewhat metallic taste; dissolves in 2500 parts boiling water and in 6667 parts cold; insoluble in anhydrous alcohol, soluble with difficulty in aqueous, scarcely soluble in ether. Quite pure strychnin dissolves in concentrated nitric acid with a yellow color; if only a trace of *brucin* be present, it is immediately colored red.

Reactions of  
strychnin.

If strychnin be rubbed in a mortar with a few drops of concentrated sulphuric acid, which contains 1 per cent. nitric acid, it vanishes without changing color; but if only a trace of superoxide of lead be poured in, there is in a moment produced a splendid blue color, which is quickly converted into violet, then into red, and, at last, into green-finch color. The same reaction also takes place, if a very small quantity of dissolved chromate of potassa be brought into a solution of strychnin in concentrated sulphuric acid; if strychnin be treated with superoxide of lead and dilute sulphuric acid, we thus obtain a brownish-yellow, bitter powder; soluble with difficulty in water and alcohol. This powder reacts acid, and completely saturates potassa. Chlorine converts strychnin into a base containing chlorine, one atom of H being replaced by one atom of chlorine. If chlorine be added to a dissolved strychnin salt, a flocculent precipitate is immediately produced.—*Bromine* behaves in like manner. The substitution affects the pairing in strychnin. By heating it with *hydrate of potassa*, it is decomposed into chinolin, hydrogen gas, and carbonic acid.

*Salts of Strychnin.* Strychnin is a strong organic base, it completely saturates acids, expels most organic bases from their compounds, and forms double salts; they possess an extremely bitter taste, and act poisonously like strychnin. The *sulphate of*

*strychnin*,  $\text{StrH}, \text{O} + \text{SO}_3$ , crystallizes in large quadrilateral prisms; the acid salt,  $\text{StrH}, \text{O} + \text{HO} + 2\text{SO}_3$ , appears in long, thin needles. The *nitrate*,  $\text{StrH}, \text{O} + \text{NO}_5$ , forms colorless needles; if it be heated with concentrated acid, thus is obtained the salt of a nitrogen base. The *hydrochlorate*,  $\text{StrH}, \text{Cl} + 3\text{aq}$ , crystallizes in needles, easily soluble in water. The *hydriodate* is insoluble in water. With perchloride of mercury, and cyanide of mercury, strychnin gives compounds  $= \text{Str} + 2(\text{HgCl}), \text{Str} + 2(\text{HgCy})$ .

*Brucin*. *Brucin* (Brucia) :  $\text{Br} = \text{N}_2\text{C}_{46}\text{H}_{26}\text{O}_8$ , is found in the false *Angustura* bark (probably the bark of *Strychnos nux vomica*), in combination with tannin, and in the fruit of the different species of *strychnos*. We obtain brucin from the false *Angustura* bark, like strychnin from Ignatius's bean. It crystallizes from the aqueous alcoholic solution by spontaneous evaporation, in colorless, transparent, quadrangular prisms; by quicker evaporation, it appears in leaflets of pearly lustre, which contain 7 atoms water. Melts at  $100^\circ$ , under loss of water. Tastes bitter, like strychnin; dissolves in 850 parts cold water, and in 500 parts of boiling; easily soluble in alcohol, insoluble in ether. In contact with *nitric acid*, it is colored red in a moment, which color is converted into violet, upon addition of chloride of tin (distinction from morphin).

If brucin be heated with nitric acid, it is said to evolve nitrate of ethyl, whilst a body remains behind which is called *Kakothelin*. *Kakothelin* :  $\text{N}_4\text{C}_{42}\text{H}_{22}\text{O}_{20}$ . However, it is possible that ethyl-amin contains brucin as its active part, and corresponds to the formula,  $\text{NC}_{42}\text{H}_{19}\text{O}_8\text{NH}_2\text{Ae}$ . This account, however, is contradicted by others. *Chlorine* converts brucin into a resinous base  $= \text{NC}_{46}\text{H}_{25}\text{BrO}_8$ . Brucin is a weaker base than strychnin and morphin, and is, by them, precipitated from its compounds. The brucin salts mostly crystallize, and taste very bitter. The *sulphate* contains 7 atoms water of crystallization, and crystallizes in long quadrilateral needles, easily soluble in water. The *nitrate* appears as a gum-like mass; the *acid nitrate* crystallizes in quadrilateral prisms, soluble in water with difficulty.

*Difference between Brucin and Strychnin*. These two bases can be easily distinguished by their behavior to nitric acid, and to superoxide of lead, to chlorine, and, further, by the fact that brucin salts, in the presence of some tartaric acid, are not precipitated by the double carbonate of potassa.

*Curarin*. *Curarin*. In *curara*, or *urari*, a substance is found which the Indians use to poison their arrows; it comes, probably, from a *strychnos*. Uncrystalline, yellowish, resinous mass; tastes bitter, and deliquesces; dissolves in all proportions in alcohol and water; insoluble in ether; reacts alkaline, and forms bitter, uncrystallizable salts. Very poisonous.



*Corydalin*:  $\text{N}_3\text{C}_{68}\text{H}_{44}\text{O}_{22}$  (?), is found in the root of *Corydalis bulbosa*, *fabacea*, and *tuberosa*. Appears as a white, inodorous, tasteless powder; soluble with difficulty in water, and rather easily soluble in alcohol and ether. It is obtained from the hot saturated alcoholic solution in prismatic crystals. *Nitric acid* colors the base, immediately, red. Reacts alkaline, and gives, with acids, very bitter salts, in part crystallizable, soluble in water and alcohol.

*Cinchonin* (Cinchona):  $\text{Ci}=\text{N}_2\text{C}_{40}\text{H}_{24}\text{O}_2$ . This base is found, in common with quinin, in the different species of cinchona bark, particularly in the gray, whilst the yellow contains more quinin. We obtain this base according to one of the above-given common methods. In order to separate the two bases, they are saturated with dilute sulphuric acid, and then so much more sulphuric acid added as is necessary to form acid salts, whose solution is evaporated to a certain point; the quinin salt is first deposited, whilst the cinchonin salt yet remains dissolved. Also, the two bases can be separated by ether, in which cinchonin is almost insoluble. The cinchonin, occurring in commerce, often contains still some chinotin admixed, from which it is separated by spontaneous evaporation of the alcoholic solution; cinchonin crystallizes first. Cinchonin crystallizes, by slow evaporation of the alcoholic solution, in thin prismatic needles; it possesses a peculiar bitter taste, dissolves in 2500 parts boiling water; dissolves particularly easy in warm alcohol, but is scarcely soluble in ether; it melts at  $165^\circ$ , and sublimes partly unchanged, when heated above its melting point; after melting, it remains as an amorphous mass (chinoidin). If we gently heat, over a spirit-lamp, dry cinchonin, in a thin layer, upon a small piece of black paper, it phosphoresces a considerable time in a dark place, with an intensive light; the solution of cinchonin bends polarized light to the right, whereby it differs from all other organic bases. If we boil cinchonin with superoxide of lead, and dilute sulphuric acid, it is changed into an amorphous bitter mass, and into *cinchonetin*. Cinchonin is a very permanent base, and resists the action of most reagents. If we add an excess of *bromine* to a solution of acid hydrochlorate of cinchonin, *bromecinchonin* is formed, in which 1 atom H is substituted by 1 atom Br. *Chlorine* gives a similar compound. Fused with *hydrate of potassa*, it decomposes into chinolin, carbonic acid, and hydrogen gas. Cinchonin reacts alkaline, and forms, with acids, very bitter, neutral, and acid salts. If the solution of the salt be slightly acidulated with tartaric acid, thus is cinchonin precipitated by double carbonate of potash, whereby it differs from quinin. *Protosulphate of cinchonin*:  $\text{CiH},\text{O}+\text{SO}_3$ , 4aq, crystallizes in prisms, with rhombic bases, dissolves in 54 parts water, and  $6\frac{1}{2}$  parts alcohol, 0.85 sp. gr.; *acid sulphate*:

Bases of cinchona bark.  
Cinchonin.



$\text{CiH}, \text{O}, \text{HO} + 2\text{SO}_3$ , crystallizes in regular octohedrons, with 15 per cent. water; dissolves in 0.46 part water, and in 0.9 part alcohol. *Hydrochlorate of cinchonin*:  $\text{CiH} + \text{Cl}$ . Easily crystallizes in shining needles, easily soluble in water and alcohol; combines with chloride of platinum, forming  $\text{CiH}, \text{Cl} + 2(\text{PtCl}_2)$ .

*Quinin*. *Quinin* (Chinin, Quinia):  $\text{Qu}(=\text{Ch}) = \text{N}_2\text{C}_{40}\text{H}_{24}\text{O}_4$ .

Production, see Cinchonin. By slow, spontaneous evaporation of the alcoholic solution, it crystallizes in silken tufts; if some ammonia be added to the alcoholic solution, we obtain it in needles. The crystals contain 1 atom water, and by gentle heat, fall into a fine powder; melts at  $150^\circ$ , and stiffens to a resin-like mass, which becomes strongly electric by rubbing; tastes more bitter than cinchonin; dissolves in 100 parts water; easily soluble in alcohol, soluble also in ether. If the solution of quinin in anhydrous alcohol be evaporated, resin-like quinin remains behind. The precipitated quinin contains 3 atoms water; it is amorphous, and becomes crystalline under loss of 2 atoms water after lying a long time in a moist condition. *Chlorine* decomposes quinin and forms a reddish, pasty, resinous mass. Fused with hydrate of potash, we obtain chinolin, carbonic acid, and hydrogen gas. If from the formula of quinin we withdraw chinolin, there remains  $2(\text{C}_2\text{H}_4\text{O}_2)$ ; this is the constitution of wood-spirit. The quinin salts all possess a very bitter taste; are, in part, soluble with difficulty in water, but easily in alcohol, and a few also in ether. Quinin is dissolved in lime-water, in ammonia, and in solution of potassa, but not in solution of soda.

*Sulphate of Quinin*:  $\text{QuH}, \text{O} + \text{SO}_3 + 18\text{aq}$ , crystallizes in long, limber, pearly needles, which are dissolved in 740 parts cold water and in 30 parts of boiling; 18 parts cold alcohol take up 1 part. The crystals effloresce in a warm place under loss of 16 atoms water. *Acid sulphate of quinin*:  $\text{QuH}, \text{O}, \text{HO} + 2\text{SO}_3 + 14\text{aq}$ , forms small acicular crystals; soluble in 11 parts cold water.

*Hydrochlorate of Quinin*:  $\text{QuH}, \text{Cl}$ , appears in needles of mother-of-pearl lustre. The platinum double salt consists of  $\text{QuH}, \text{Cl} + \text{PtCl}$ .

*Chinotin* ( $\beta$ . quinin). This base has the same constitution as quinin. Is found sometimes in chinoidin (amorphous quinin), and can be extracted from the same by ether. Crystallizes from the etheric solution in large columns, which become opaque in the air, without falling to pieces; is dissolved in 1500 parts water, in 45 parts absolute alcohol, and in 90 parts ether; and forms with acids neutral and acid salts of very bitter taste. Part of these salts are soluble with difficulty, like the corresponding quinin salts.

*Chinidin*. This base appears to occur in *China huamallies*. Crystallizes from the alcoholic solution in large, direct, four-sided columns of glassy lustre, and is, probably, identical with chinotin.

*Chinoidin* (Amorphous Quinin). This body remains Chinoidin. in the production of quinin in a large way, at last, as a resinous body. It is an isomeric modification of quinin in which it has lost the property of crystallizing, and in which quinin and chinotin are often admixed. Medicinally, it acts when pure like quinin.

*Aricin*:  $\text{Ar} = \text{N}_2\text{C}_{40}\text{H}_{24}\text{O}_6$ , is found in the Aricin. so-called *Arica* bark, whose origin is unknown. Crystallizes in white, shining, transparent needles; insoluble in water, soluble in alcohol and ether; inodorous, and possesses a taste bitter, and after a little time burning and itching. The salts are soluble in water and alcohol, but not in ether; they easily crystallize, and taste bitter.

*Pelosin* (Cisampeline):  $\text{NC}_{36}\text{H}_{21}\text{O}_6$ , is found in the Pelosin. American gravel root, *Radix pareiræ bravæ* (*Cisampelos pareira*). From the etheric solution pelosin remains as a yellow, transparent, amorphous mass; in contact with water, it absorbs 3 atoms of that liquid. Inodorous; tastes repulsively sweetish; insoluble in water, easily soluble in alcohol and ether; extremely easily decomposable. A strong base, which neutralizes the most powerful acids. The salts are mostly easily soluble, and dry to a brittle, transparent, amorphous mass.

*Berberin*:  $\text{Be} = \text{NC}_{42}\text{H}_{18}\text{O}_9$ , is found in the root of Berberin. *Berberis vulgaris* and in *Columbo* root. Is obtained if the watery extract be treated with alcohol of 82 per cent., until it no longer has a bitter taste, the alcohol distilled off, and the residue left standing some time in a cool place. Berberin crystallizes in fine yellow needles, which dissolve in water with a dark-red color, and contain 12 atoms water of crystallization, of which 10 atoms escape at  $100^\circ$ . Berberin, with most inorganic acids, gives compounds soluble with difficulty, the hydrochlorate alone is rather easily soluble; the salts possess a yellow color, and a capability of crystallizing. The base gives *chinolin* by distillation with milk of lime.

*Harmalin*:  $\text{Ha} = \text{N}_2\text{C}_{27}\text{H}_{14}\text{O}_2$ . This base is found Harmalin. in the seed of *Peganum harmala*, a weed growing in the southern Russian steppes. Crystallizes in yellowish, transparent, rhombic columns; tastes slightly bitter, afterwards somewhat sharp; colors the saliva lemon-yellow; soluble with difficulty in water and alcohol, more easily soluble in ether. The salts of harmalin are yellow, the greater part easily soluble, in part crystallizable.

*Harmin*:  $\text{N}_2\text{C}_{27}\text{H}_{12}\text{O}_2$ . This base is found in Harmin. harmala seed, and is formed from harmalin, if the latter yields  $\text{H}_2$ . If we heat nitrate of harmalin with a mixture of equal parts alcohol and hydrochloric acid, by cooling off suddenly, hydrochlorate of harmin is precipitated. This is dissolved

in water, and the harmin precipitated by an alkali. Colorless, brittle, shining, rhombic columns, strongly refracting light. Is dissolved in water, alcohol, and ether, like harmalin, and forms colorless, purely bitter-tasting salts, from whose solution the base is precipitated by an alkali, at first oily, but after some time stiffens crystalline. The salts crystallize.

*Nitroharmalin*:  $N_2C_{27}H_{13}O_{27}NO_4$ , forms light-yellow, very fine prismatic needles; slightly soluble in cold water, more easily soluble in hot; easily soluble in alcohol and hot ether; gives, with bases, yellow crystallizable salts. Is formed by the action of nitric acid upon harmalin.

*Hydrocyanide of Harmalin*:  $N_2C_{27}H_{14}O_2CyH$ . A salt of harmalin is decomposed by cyanide of potassium, whereby we obtain an amorphous precipitate, which crystallizes from the alcoholic solution, and by boiling with water decomposes into hydrocyanic acid and harmalin. It behaves like a base and forms colorless salts, which, however, easily decompose into harmalin salts and hydrocyanic acid.

*Bebeerin*:  $Be=NC_{35}H_{20}O_6$ . This base is found in the bark of a tree, which is known under the name of bebeeru or *green-heart* of Demarara. Appears as a light-yellow, uncrystalline, amorphous mass; soluble in 6650 parts water, in 5 parts alcohol, and in 13 parts ether; tastes bitter; reacts strongly alkaline, and forms with acids uncrystallizable yellow salts.

*Piperin*:  $N_2C_{70}H_{37}O_{10} + 2HIO$ , is found in black, in white, and in long pepper. Pepper is extracted with alcohol, then the alcohol distilled off, and the resin extracted from the residue by potassa; the piperin remains and is purified by recrystallization from the alcoholic solution. Crystallizes in white, transparent, quadrilateral needles, without odor or taste, and almost insoluble in cold water, but easily soluble in alcohol, ether, and fatty oils. Piperin does not react alkaline. If hydrochloric acid and chloride of platinum be added to a concentrated alcoholic solution of piperin, we obtain, by spontaneous evaporation, large dark orange-red crystals  $= N_2C_{70}H_{37}O_{10}HCl + PtCl_2$ .

If we heat an intimate mixture of piperin with soda-lime to  $150^\circ$ , picolin goes over, and as residue remains a resinous body, whose constitution can be expressed by  $N_3C_{128}H_{67}O_{20}$ . Now 2 atoms of piperin  $= N_4C_{140}H_{74}O_{20} - NC_{12}H_7 = N_3C_{128}H_{67}O_{20}$ . Piperin may, therefore, be considered a paired compound of piperin with a body  $= NC_{58}H_{30}O_{10}$ .

Besides the already treated paired bases, there is still a large number known, which, however, require a more particular investigation, as *pereirin*, which is procured from the bark of a Brazilian tree, of the genus *Cerbera*. *Pitoyin* is found in *China pitoya*.

Bases not yet particularly investigated.

*Menispermin*:  $\text{NC}_{18}\text{H}_{12}\text{O}_2$ , is found in shells of *Cocculus indicus*.

*Capsicin* is found in the seed-case of *Capsicum annum*.

*Surinamin* occurs in the bark of *Geoffroya surinamensis*.

*Jamaicin* is obtained from *Geoffroya jamaicaensis*, etc. (Compare my "Chemistry of Organic Combinations.")

### Second Group.

#### PHOSPHORUS BASES.

The phosphorus bases now known are:—

Biphosmethyl . . . .	$\text{P Me}_2$ ,
Phosbimethyl . . . .	$\text{P}^2\text{Me}_2$ ,
Phosmethylamin . . . .	$\text{PH}_2\text{Me}$ ,
Phostrimethyl . . . .	$\text{P Me}_3$ .

These compounds are formed by the action of chloride of methyl upon phosphide of calcium, at high temperature.

*Biphosmethyl* (Biphosphide of Methyl):  $\text{P}_2\text{Me}$ . If phosbimethyl be a long time exposed to the action of hydrochloric acid gas, it decomposes into biphosmethyl and phostrimethyl. The former is a yellow, non-volatile, inodorous, and tasteless body.

*Phosbimethyl* (Diphosphide of Methyl):  $\text{PMe}_2$ , appears as a colorless, transparent fluid, insoluble in water, extremely bad smelling, boils at  $250^\circ$ , spontaneously inflames in the air, and, by slow oxidation, is converted into a crystallizable acid. With hydrochloric acid gas this base forms, at first, a solid, durable, crystallizable combination; by farther action of the gas, we obtain fluid acid, less durable, which, at last, decomposes into biphosmethyl and phostrimethyl. The crystallizable hydrochloric acid combination dissolves in water at  $0^\circ$ , unchanged; but, if the solution be warmed, it divides, under decomposition of water, into an acid, which is also formed by oxidation of phostrimethyl.

*Phosmethylamin* (Phosphide of Methylamin):  $\text{PH}_2\text{Me}$ , exhibits a spontaneously inflammable gas, which unites with hydrochloric acid gas, forming a solid combination; in contact with water, this compound is divided, instantly, into hydrochloric acid and phosmethylamin gas. With an equal volume of oxygen, this body forms a very sour fluid.

*Phostrimethyl* (Triphosphide of Methyl):  $\text{PMe}_3$ . An extremely strong basic fluid, which boils at  $40^\circ$ , and, by oxidation, is converted into an acid.

The corresponding ethyl compounds are said to be formed by the action of chloride of ethyl upon phosphide of calcium.



*Third Group.*

## ARSENIC BASES.

The bases of this group, at present known, are Arsenic-bimethyl, or Kakodyl:  $\text{AsMe}_2$ , whose oxide is formed by dry distillation of an intimate mixture of acetate of potassa with arsenious acid, and arsenethyl,  $\text{AsAe}$ .

*Kakodyl.* *Kakodyl:*  $\text{AsMe}_2 = \text{Kd} = 2$  volumes gas. Pure kakodyl is obtained when perfectly pure chloride of kakodyl is exposed, for a few hours, with plate-zinc, to a temperature of  $100^\circ$ . After the termination of the decomposition, we obtain a white, porous salt mass, which is warmed—the air being completely excluded. Kakodyl collects, at the bottom, as an oily liquid, and is purified by distillation over zinc. Water-clear, thin-flowing liquid, strongly refracting light, and, at  $-6^\circ$ , crystallizing in large quadratic prisms; boils at  $170^\circ$ . In spontaneous combustibility it excels all bodies yet known. Divides at  $400^\circ$  to  $500^\circ$  into arsenic, marsh gas, and elayl gas, without deposition of carbon. If it be a long time digested with hydrochloric acid and metallic tin, or with phosphorous acid, we obtain, besides other products, *erytrarsin*,  $= \text{AsMe}_2 + \text{As}_2\text{O}_3$ . Kakodyl combines directly with O, S, the halogens, etc.

*Oxide of Kakodyl:*  $= \text{KdO}$ . An intimate mixture of arsenious acid and acetate of potassa is submitted to dry distillation, the air being completely excluded, and the distillate collected in a receiver surrounded by ice. We obtain an oily fluid, almost solely consisting of oxide of kakodyl, which, separated from the excess of water present, is several times washed with water, and, at last, repeatedly distilled by itself, and then over lime. Since a quantity of poisonous gas is evolved, all the operations must be conducted with great caution, and with complete exclusion of air. Colorless, water-clear, etheric liquid, strongly refracting light, insoluble in water, miscible in all proportions with alcohol and ether; crystallizes under  $-23^\circ$ , possesses a highly repugnant odor, exciting, even in slightest quantity, to tears, and produces an almost insupportable irritation upon the mucous membrane of the nose; tastes disagreeably, and acts poisonously internally. Sp. gr. 1.642; boils at  $150^\circ$ . Extremely easily inflamed.

*Oxide of kakodyl* is a real base, and combines directly with acids, forms salts, which, in part, crystallize. If we add a dilute solution of nitrate of silver to a solution of *nitrate of kakodyl*, we obtain a white crystalline precipitate which consists of  $3\text{KdO} + \text{AgO}, \text{NO}_5$ .

*Kakodylic Acid*:  $\text{HO, KdO}_3$ . If, to refrigerated oxide of kakodyl, we let oxygen slowly enter through a fine opening, we thus obtain arsenious acid, oxide of parakakodyl, and kakodylic acid. Oxide of kakodyl reduces oxide of mercury, of silver, of gold, etc. If, under a stratum of water, we bring oxide of kakodyl, together with oxide of mercury, we obtain, under deposition of metallic mercury, a solution of kakodylate of mercury, and if to this we add oxide of kakodyl, in drops, so long as mercury is precipitated, we thus obtain, by evaporation of the solution, pure kakodylic acid. Crystallizes from the alcoholic solution, in large, well-formed, brittle, transparent, sourish-tasting crystals, deliquescent in the air. Dissolves in water and ordinary alcohol, in all proportions, and resists the action of the most powerful reagents. Phosphorous acid and zinc reduce kakodylic acid into oxide. Kakodylic acid combines with bases to form salts, which are all soluble in water, and, in part, are obtained in crystals from the alcoholic solution. With oxide of silver it gives a neutral and an acid salt, which last consists of  $\text{AgO, 2HO, 3KdO}_3$ . Also double salts are known.

*Protosulphide of Kakodyl*:  $\text{KdS}$ . If a solution of  $\text{BaS, H}_2\text{S}$  be distilled with chloride of kakodyl, thus, under evolution of hydrosulphuric acid, the sulphide of kakodyl goes over as a water-clear etheric fluid; not fuming in the air; of highly disagreeable smell; is not solid, even at  $-40^\circ$ ; boils at  $100^\circ$ ; insoluble in water; miscible in all proportions with alcohol and ether. *Sulphokakodylic Acid*:  $\text{KdS}_3$ . If in 1 atom of protosulphide of kakodyl, we dissolve 2 atoms sulphur; the fluid stiffens, after cooling, to a mass of crystalline scales. If these are dissolved in absolute alcohol, we obtain, under deposition of sulphur,  $\text{KdS} + \text{KdS}_3$ . Sulphokakodylic acid forms sulphur salts with sulphur bases. These are obtained by precipitation of the kakodylates with hydrosulphuric acid, as well as by decomposition of *sulphokakodylate of sulphide of kakodyl*,  $\text{KdS} + \text{KdS}_3$ , with metallic salts. The combination  $\text{KS} + \text{KdS}_3$ , by slow cooling, crystallizes in large water-clear, rhombic, fatty tables; unchangeable in the air, and smelling like asafetida; melts at  $50^\circ$  to a colorless liquid; easily soluble in alcohol, soluble with difficulty in ether, insoluble in water; mercury immediately reduces the combination into  $\text{KdS}$ , under production of sulphide of mercury.

*Selenium* behaves to kakodyl like sulphur.

*Protochloride of Kakodyl*:  $\text{KdCl}$ , is obtained, if bichlorokakodyl-mercurioxyd,  $\text{Hg}_2\text{O} + \text{KdCl}_2$  (*vide* below), be distilled with highly concentrated hydrochloric acid. (If oxide of kakodyl be treated with hydrochloric acid, we obtain as secondary product, erytrarsin also.) Water-clear, etheric liquid; boils above  $100^\circ$ , and, as a gas, it inflames spontaneously; does not fume, but diffuses a

Kakodylic acid.

Kakodyl and sulphur.

Kakodyl and halogens.

Kakodyl and chlorine.

penetrating, benumbing odor, and acts uncommonly exciting upon the mucous membrane of the nose; insoluble in water and ether; easily miscible with alcohol. If we leave chloride of kakodyl in contact with the air, beautiful large crystals are formed. Chloride of kakodyl forms with *dichloride of copper*, *chloride of platinum*, and other *chlorine compounds* a large number of double salts.

If dry hydrochloric acid gas be conducted into pure oxide of kakodyl, under complete exclusion of the air and artificial refrigeration, we obtain two layers; the upper is chloride of kakodyl, the lower consists of  $\text{KdCl} + \text{HO}$ , or *aqueous chloride of kakodyl*; it forms a tenacious thick-flowing mass, from which the water can be absorbed by chloride of calcium.

*Oxychloride of Kakodyl*:  $\text{KdO} + 3\text{KdCl}$ , is formed by bringing together chloride of kakodyl and water, or by dry distillation of oxide of kakodyl with aqueous hydrochloric acid. Resembles almost exactly the chloride of kakodyl, but fumes in the air.

*Bichloride of Kakodyl*:  $\text{KCl}_2$ , is not known isolated. But if we add a dilute solution of bichloride of mercury to a dilute alcoholic solution of potassa, a white, voluminous precipitate is formed of calomel and  $\text{Hg}_2\text{O} + \text{KdCl}_2$ . If we treat this precipitate with boiling water, the last compound is dissolved, and, by cooling, is deposited in large, brittle, satin-lustred scales.

If we treat this *bichlorkakodyl-mercurydioxyd* (bichloride of kakodyl and dioxide of mercury) with phosphorous acid or with hydrochloric acid, we obtain calomel and protochloride of kakodyl. A combination of *kakodylic acid* with *bichloride of kakodyl*  $= \text{KdO}_3 + 3\text{KdCl}_2$ , is obtained if aqueous terchloride of kakodyl,  $\text{KdCl}_3 + 3\text{HO}$ , be gently heated, until a perceptible blackening takes place, after which the obtained oily distillate is deprived of water by caustic baryta. An extremely irritating compound, which, in energy, surpasses all other compounds of kakodyl.

*Terchloride of Kakodyl* (Superchloride of Kakodyl):  $\text{KdCl}_3 + 3\text{HO}$  (?). If dry hydrochloric acid gas be conducted over dry kakodylic acid, we obtain, without separation of water, a fluid, in which, by cooling, crystals of oxychlorkakodylic acid shoot. The fluid separated from the crystals is terchloride of kakodyl; it is syrup-thick, water-clear, inodorous; slightly fuming; decomposes by gentle heating into chloride of methyl, arsenious acid, and  $2\text{KdO}_3 + 3\text{KdCl}_2$ . Zinc, by degrees, completely reduces the compound to kakodyl. *Oxychlorkakodylic acid*,  $2\text{KdO}_3 + \text{KdCl}_3 + 6\text{H}$   
 $\text{O} = \text{Kd} \left\{ \begin{array}{l} \text{O} \\ \text{Cl} \end{array} \right. + 2\text{HO}$ , is deposited in large, white, transparent, inodorous, very acid crystal leaflets, if a solution of kakodylic acid in most highly concentrated hydrochloric acid be evaporated in a vacuum; decomposes at a high temperature into chlormethyl, and  $2\text{KdO}_3 + 3\text{KdCl}_2$ . If an alcoholic solution of corrosive sublimate be added to an alcoholic solution of kakodylic acid, white, inodor-



ous crystals are formed, which are soluble in water in every proportion, and can be regarded as constituted of  $2\text{HgO} + \text{KdCl}_3 + \text{H}_2\text{O}$ .

*Protobromide of Kakodyl*:  $\text{KdBr}$ , is obtained if  $\text{Hg}_2\text{O} + \text{KdCl}_3$ , be distilled with most highly concentrated hydrobromic acid. Resembles chloride of kakodyl, and, in contact with water, decomposes into hydrobromic acid and oxybromide of kakodyl (oxybromkakodyl):  $\text{KdO} + 3\text{KdBr}$ . If, to an alcoholic solution of oxide of kakodyl, we add a solution of simple bromide of mercury, we obtain  $\text{Hg}_2\text{Br}$  and  $\text{Hg}_2\text{O} + \text{KdBr}_2$ . Kakodyl and bromine.

*Terbromide of Kakodyl*:  $\text{KdBr}_3$ , is not known isolated. If we distil kakodylic acid with pure concentrated hydrobromic acid, we obtain a colorless, tenacious, inodorous, completely neutral fluid, which consists of  $\text{KdO}_3 + 3\text{Kd} \left\{ \begin{smallmatrix} \text{O}_3 \\ \text{Br} \end{smallmatrix} \right.$ , and, by heating, decomposes into bromide of methyl, into  $2\text{KdO}_3 + 3\text{KdBr}_2$ , and into arsenious acid.

*Iodide of Kakodyl*:  $\text{KdI}$ . We distil oxide of kakodyl with concentrated hydriodic acid. The distillate consists of iodide of kakodyl and oxyiodide of kakodyl, which last is deposited, if the mixture be strongly refrigerated. Iodide of kakodyl is thin-flowing, yellowish, and of disgusting, irritating, penetrating odor, insoluble in water, easily soluble in alcohol and ether. *Oxyiodide of kakodyl*:  $\text{KdO} + 3\text{KdI}$ , crystallizes in yellowish, transparent rhombic tables, fumes in the air, inflames spontaneously, has a great affinity for oxygen, and is not changed into iodide of kakodyl, either by digestion or by distillation with hydriodic acid. Kakodyl and iodine.

*Fluoride of Kakodyl*:  $\text{KdFl}$ , is obtained like chloride of kakodyl. Colorless fluid, insoluble in water, and of most disgusting odor. *Oxyfluor-kakodylic acid*:  $\text{Kd} \left\{ \begin{smallmatrix} \text{Fl} \\ \text{O} \end{smallmatrix} \right. + \text{HO}$ , is obtained by dissolving kakodylic acid in hydrofluoric acid. Forms long, transparent, inodorous prismatic crystals, easily soluble in water and alcohol.

*Arsenethyl (Arsenic-Ethyl)*:  $\text{AsC}_4\text{H}_5 = \text{AsAe}$ . If we bring an alcoholic potassa solution in contact with chloride of kakodyl, we obtain chloride of potassium, water, and arsenethyl. The compound exhibits, in anhydrous condition, a water-clear, very thin-flowing liquid, of disgusting etheric odor; is volatile like ether, and mixes with alcohol and water in all proportions. Ethyl and arsenic.

*Aminoxide of Arsenethyl (Parakakadyloxyd)*:  $= \text{As} \left\{ \begin{smallmatrix} \text{H} \\ \text{Ae} \end{smallmatrix} \right. \text{O} = \text{AsC}_4\text{H}_6\text{O}$ , is formed, in addition to kakodylic acid, by direct oxidation of oxide of kakodyl. We obtain a mixture of kakodylic



acid with kakodylate of kakodyl. If the last compound be distilled at  $120^{\circ}$ , the aminoxide of arsenethyl goes over. Resembles, in many respects, oxide of kakodyl, but does not fume in the air, and is oxidized only with difficulty. The compounds are, also, different from those of oxide of kakodyl.

*Erytrarsin*:  $\text{As}_3\text{C}_4\text{H}_6\text{O}_3 = \text{AsMe}_2 + \text{As}_2\text{O}_3 = \text{As} \left\{ \begin{matrix} \text{H} \\ \text{Ae} \end{matrix} + \text{As}_2\text{O}_3 (?) \right.$

It is formed as secondary product, if the vapor of kakodyl and of oxide of kakodyl are conducted through a gently heated tube, yet in small quantity; also a little is formed during the production of chloride of kakodyl. A changeable steel-blue and dark-red mass, almost inodorous, without any trace of crystallization; ground, it forms a brick-red powder, insoluble in water, alcohol, and ether.

#### *Fourth Group.*

#### ANTIMONY BASES.

The antimony bases, at present known, are : —

Stibmethyl . . .	$\text{StMe}_3$ ,
Stibmethylium . . .	$\text{StMe}_4$ ,
Stibethyl . . .	$\text{StAe}_3$ ,
Stibethylium . . .	$\text{StAe}_4$ ,
Stibamyl . . .	$\text{StAm}_3$ .

Production of antimony bases and a few of their general properties.

The compounds,  $\text{StMe}_3$ ,  $\text{StAe}_3$ , and  $\text{StAm}_3$ , are obtained by distillation of iodide of methyl, of ethyl, or of amyl, with antimony-potassium. On account of the readiness with which these compounds oxidize, all the operations, as in the production of kakodyl, must be conducted under complete exclusion of air, and in a current of carbonic acid. These compounds have an extraordinary power of combination, and unite, at common temperature, with oxygen, sulphur, selenium, and the halogens, under perceptible evolution of heat, which suddenly rises to inflammation, with stibmethyl and stibethyl. The combinations with the above-named elements agree, in all respects, with those of potassium, and may be converted into each other by double decomposition; the basic radicals mentioned, combine only with  $\text{O}_2$ ,  $\text{S}_2$ ,  $\text{Cl}_2$ , etc., whereby they also differ, as already stated above, from kakodyl. The combination, with 4 atoms methyl, or ethyl, quite agrees with ammonium; they unite only with 1 atom O, S, Cl, etc. We obtain these compounds by the action of iodide, or bromide of methyl, or ethyl, upon stibmethyl, or stibethyl, in which case the haloid compounds  $= (\text{StMe}_4)\text{I}$ ,  $(\text{StAe}_4)\text{I}$ , etc., are formed.

*Stibmethyl*:  $\text{StMe}_3$ . This compound exhibits a colorless, heavy fluid, which strongly refracts light, and, in all respects, agrees with the more accurately investigated stibethyl; therefore we refer to that substance. Stibmethyl.

*Stibmethylium*:  $\text{StMe}_4$ . The pure compound is not yet known. Stibmethylium.

*Oxide of Stibmethylium*:  $(\text{StMe}_4)\text{O} + \text{HO}$ . We obtain this body, if iodide of stibmethylium  $(\text{StMe}_4)\text{I}$ , in aqueous solution, be shaken with freshly precipitated oxide of silver, and the fluid, filtered from the iodide of silver, be evaporated, in a vacuum, over sulphuric acid. A white, crystalline, extremely caustic, and alkaline-tasting mass, which, in all respects, agrees with hydrate of potassa; easily soluble in water and alcohol, scarcely soluble in ether. Volatilizes at a high temperature, unchanged. Warmed with potassium, a spontaneously inflaming gas is evolved. This base completely saturates acids, and, with them, gives salts, which quite agree with potassa salts, and expels ammonia, baryta itself, and lime, as well as the oxides of all heavy metals, from their combinations. The precipitates formed in the salts of alumina and oxide of zinc, are dissolved in an excess of the precipitants. From copper salts, oxyhydrate of copper is precipitated, which an excess of the base does not again dissolve; in like manner, it dissolves no trace of oxide of silver. All the salts possess a bitter taste. Its combina-  
tions.

*Sulphate of Stibmethylium*:  $(\text{StMe}_4)\text{O}, \text{SO}_3$ , is obtained, if sulphate of silver be added to the alcoholic solution of the iodine compound, and the solution, filtered from the iodide of silver, be mixed with a quantity of ether and alcohol. The salt separates oily, but very soon stiffens in rhombic crystals; if a solution of the neutral salt be evaporated upon the water-bath, we obtain the acid salt:  $(\text{StMe}_4)\text{O}, \text{HO} + 2\text{SO}_3$ , in hard crystals, which react acid.

*Bicarbonate of Stibmethylium*:  $(\text{StMe}_4)\text{O}, \text{HO} + 2\text{CO}_2$ , we obtain crystalline, if a solution of the pure base be completely saturated with carbonic acid; unchangeable in the air, and easily soluble in water. *Iodide of stibmethylium*:  $(\text{StMe}_4)\text{I}$ , forms beautiful white, inodorous, bitter-tasting crystals, soluble in water and alcohol, in the same manner as the *chlorine compounds*.

*Iodide of Stibmethylethylum*:  $(\text{StMe}_3\text{Ac})\text{I}$ , is obtained, if iodide of ethyl be added to stibmethyl; quite equals iodide of stibmethylium.

*Stibethyl*:  $\text{StAc}_3 = 4$  volumes gas. Appears as a water-clear, extremely thin-flowing liquid, strongly refracting light; of disagreeable, onion-like odor, which, however, soon vanishes; is not solid at  $-29^\circ$ ; insoluble in water, easily soluble in alcohol and ether; boils at  $158.5^\circ$ ; sp. gr. 1.3244. Stibethyl.

*Oxide of Stibethyl:*  $(\text{StAe}_3)_2\text{O}_2 + 2\text{HO}$ . If we bring a jet of stibethyl into oxygen gas, it inflames instantly, and burns with dazzling white light; the same also occurs in the air, only the inflammation takes place after a few seconds, a thick white smoke arising previously. If, however, the oxidation takes place slowly, we obtain a transparent, syrup-thick mass, which presents a combination of oxide of stibethyl, with antimonite of stibethyl:  $(\text{StAe}_3)_2\text{O}_2 + 2\text{StO}_3$  (the so-called ethylstibethylic acid). We obtain the oxide pure, if we precipitate the sulphuric acid salt with baryta water, and from the abfiltered solution, precipitate the yet dissolved baryta by carbonic acid. After evaporation, the oxide remains as a tenacious, perfectly water-clear, transparent mass, without a trace of crystallization. Easily soluble in water and alcohol, soluble with difficulty in ether; tastes bitter, not poisonous, and produces no vomiting; not volatile. Oxide of stibethyl behaves like an inorganic base, and, with acids, gives crystallizable salts, easily soluble in water.

*Sulphate of Stibethyl:*  $(\text{StAe}_3)_2\text{O}_2 + 2\text{SO}_3$ , is obtained by decomposition of sulphide of stibethyl with sulphate of copper. Forms small, white, inodorous, acid-reacting, bitter-tasting crystals, soluble in water and alcohol.

*Nitrate of Stibethyl:*  $(\text{StAe}_3)_2\text{O} + 2\text{NO}_5$ . When stibethyl is brought together with fuming nitric acid, it inflames with an explosion. In dilute acid it dissolves like a metal under evolution of nitrous-oxide gas. Forms from the aqueous solution by spontaneous evaporation, in large, transparent, rhomboidal crystals, which are easily soluble in water and alcohol, react acid, taste bitter, and melt at  $62.5^\circ$ . Detonates by heating.

*Sulphide of Stibethyl:*  $(\text{StAe}_3)_2\text{S}_2$ . If we boil an etheric solution of stibethyl with washed flowers of sulphur, and pour the warm etheric solution off from the excess of sulphur, thus, after a few minutes, the fluid stiffens to a heap of dazzling white crystal needles, which smell like mercaptan, easily dissolve in water, and melt above  $100^\circ$  to a colorless fluid. If, into fused sulphide of stibethyl, we bring a piece of potassium, in a moment vapor of stibethyl is evolved. The solution of sulphide of stibethyl precipitates all metal salts as sulphides of metals; dilute acids, evolve hydrosulphuric acid instantly; non-volatile. Gives, with  $\text{StS}_3$ , a yellow insoluble compound,  $(\text{StAe}_3)_2\text{S}_2 + 2\text{StS}_3$ , smelling like mercaptan.

*Selenium* behaves to stibethyl quite like sulphur.

*Iodide of Stibethyl:*  $(\text{StAe}_3)_2\text{I}_2$ . We add iodine in small quantities to an alcoholic solution of stibethyl, until the color no longer vanishes, and evaporate the alcoholic solution. Crystallizes in completely colorless, long needles; smells slightly; tastes bitter; is easily dissolved in water,

alcohol, and ether; melts at  $70^{\circ}$ ; may be, with caution, sublimed. Behaves towards chlorine, bromine, acids, and metallic salts like iodide of potassium; nitrate of silver immediately gives a precipitate of iodide of silver.

*Bromide of Stibethyl*:  $(\text{StAe}_3)\text{Br}_2$ . If we let bromine, in drops, fall into stibethyl, each time inflammation takes place. If to an alcoholic solution, which is to be kept cold, we add bromine in small quantities so long as the color vanishes, and then mix the solution with a large quantity of water, bromstibethyl is thus separated as a completely colorless water-clear fluid, which, at  $-10^{\circ}$ , stiffens to a snow-white, crystalline mass; smells disagreeably like turpentine; excites, by warming, strongly to tears; insoluble in water, easily soluble in alcohol and ether; non-volatile, and behaves, chemically, quite like bromide of potassium. Stibethyl and bromine.

*Chloride of Stibethyl*:  $(\text{StAe}_3)\text{Cl}_2$ . If we let stibethyl fall from a narrow tube into a balloon filled with chlorine, it is inflamed at the moment of contact. Hydrochloric acid gas is decomposed by stibethyl under evolution of hydrogen and formation of chloride of stibethyl; the same follows, when concentrated hydrochloric acid is poured over stibethyl. If we mix a solution of nitrate of stibethyl with a strong hydrochloric acid, chloride of stibethyl is immediately separated as a colorless fluid; strongly refracting light; smells like turpentine; tastes bitter; is insoluble in water, easily soluble in alcohol and ether; is fluid, even at  $-12^{\circ}$ ; sp. gr. 1.540; not volatile; behaves chemically quite like chloride of potassium. Stibethyl and chlorine.

*Stibethylium*:  $\text{StAe}_4$ . At present, only the iodine combination is known,  $(\text{StAe}_4)\text{I}$ , which is obtained, if iodide of ethyl be added to stibethyl. Crystallizes in beautiful long needles, which are easily soluble in water and alcohol. Stibethylium.

*Stibamyl*:  $\text{StAm}_3$ , appears as a clear, colorless fluid, which fumes in the air, but does not inflame, and forms the same combinations as stibethyl; only all the compounds are fluid, and insoluble in water. Stibamyl.

*Bismæthyl* (Bismuth-Ethyl):  $\text{BiAe}_3$ . Bismæthyl is obtained in a similar manner to stibethyl, under the employment of bismuth-potassa. It exhibits a pale-yellow, very thin-flowing liquid of 1.80 sp. gr., distillable only with water. Smells disagreeable like stibethyl, and produces, when only a trace is inhaled, a highly disgusting burning sensation upon the tongue. In the air, it diffuses thick vapors, and inflames under emission of copious yellow fumes of oxide of bismuth. With oxygen, the halogens, and sulphur, it combines in the same proportions as stibethyl, only the combinations are less permanent; if we leave, e. g. the alcoholic solution of bismoethyl some time standing, pure iodide of bismuth is deposited. Heated alone, it Bismæthyl.



decomposes, under deposition of bismuth and evolution of a gaseous product; suddenly exposed to a high temperature, it explodes with great violence.

Platinum bases. *Platinum Bases.* By the action of ammonia upon protochloride of platinum, bases are formed, which correspond to the formulæ  $\text{NH}_2\text{Pt}$  and  $\text{N}_2\text{H}_3\text{Pt}$ . The first combination may be considered as ammonia, in which H is replaced by Pt, the second compound is then constituted according to the formula  $(\text{NH}_2\text{Pt} + \text{NH}_3)$ . Similar bases also arise by the action of methylamin and ethylamin upon protochloride of platinum. Thus protochloride of platinum, in a concentrated solution of methylamin, changes into a green powder, which is insoluble in water, and consists of 1 atom methylamin,  $\text{NH}_2\text{C}_2\text{H}_3$  and  $2\text{PtCl}$ . If this combination be some time heated with excess of methylamin in a stopped flask over the water-bath, we thus obtain crystals, which consist of  $\text{N}_2\text{C}_4\text{H}_9\text{Pt} + \text{HCl} = (\text{NH}_2\text{C}_2\text{H}_3 + \text{NH}_2\text{Pt}, \text{C}_2\text{H}_3)\text{Cl}$ . Without doubt a base also exists  $= \text{NH}_2\text{Pt}, \text{C}_2\text{H}_3 = \text{NC}_2\text{H}_4\text{Pt}$ .

## SIXTH DIVISION.

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### ORGANIC COMBINATIONS OF HIGHER ORDER, WHOSE RATIONAL FORMULÆ ARE NOT YET KNOWN.

#### a. SPECIAL COMBINATIONS OF THE VEGETABLE KINGDOM.

##### *First Group.*

##### TANNIN, OR TANNIC ACID.

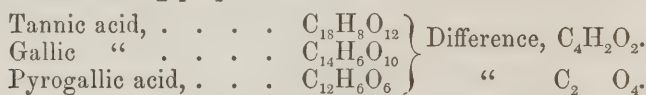
IN many plants, particularly the perennial, organic compounds are found, which possess a very astringent taste, and, on account of their property of forming leather with the skins of animals have obtained the name of "*tannin*," or, also, on account of their weak acid properties, "*tannic acid*." Almost without exception they are amorphous; they precipitate most metallic oxides from the solution of their salts; give, with the salts of peroxide of iron, blackish blue or grayish green precipitates; with the bases of organic salts, with glue and the protein substances, they give insoluble compounds. They are more or less completely precipitated from their solution by mineral acids, and give, with those acids, compounds soluble in pure water. They are easily soluble in water and alcohol, in part also in ether, and in their perfectly dry state they suffer no change; in their aqueous solution, on the contrary, they are mostly easily decomposed, partly by ferments, partly by absorption of oxygen, as well as by the action of dilute acids and alkalies, under simultaneous production of acetic acid, and deposition of new acids; mostly soluble with difficulty in cold water. Thus tannic acid decomposes into gallic acid; and if we heat gallic acid to 210 or 220°, it decomposes into carbonic acid and pyrogallie acid. As gallic acid relates to tannic acid (gall-nut tannin), catechuic acid relates to catechu tannin, the morinic acid to morin tannin, and the quercitronic acid to quercitron tannin. Catechuic acid leaves, by dry

Occurrence and some of the general properties of the tannins.

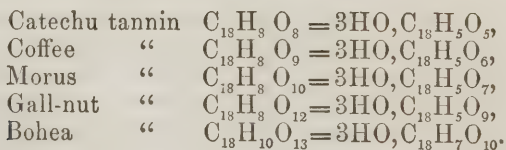
Their constitution.

distillation, pyrocatechuic acid, and the quercitronic acid leaves pyroquercitronic acid. If we treat tannins with oxidizing bodies, as with nitric acid, chromic acid, the superoxides, farther with chlorine or bromine, they are completely destroyed, under production of formic and oxalic acid. The solutions in excess of alkalies absorb oxygen with extreme rapidity, and assume a dark color under formation of new products, a behavior which belongs also to all substances which arise from the decomposition of the tannins.

From all these circumstances, as well as from their high atomic weight, and from the fact that they possess no acid properties corresponding to the oxygen they contain, it appears evident that the tannin compounds exhibit higher orders, and, without doubt, consist of several complex atoms, by whose separate escape the products of decomposition are determined. If we compare tannic acid with gallic acid, and gallic acid with pyrogallic acid, thus are given the following proportions:—



If we regard the measure of tannic acid as constituted of the molecules,  $C_4H_2O_2 + C_2O_4 + C_{12}H_6O_6$ , then must it be converted into gallic acid by losing  $C_4H_2O_2$ , and this into pyrogallic acid by loss of  $C_2O_4$ . But now tannic acid saturates 3 atoms base, it contains therefore 3 atoms basic water; hence its formula is  $3HO, C_{18}H_5O_9 = 3HO, C_4HO, C_2O_4, C_{12}H_4O_4$ . If the atom group,  $C_4HO$ , unites with the elements of 2 atoms water, we obtain acetic acid,  $C_4H_3O_3$ , and  $C_2O_4$  furnishes, after the external action, carbonic acid, formic acid, etc.\* The same relations exist between catechu, tannin, and catechuic acid; morus tannin and morinic acid; coffee tannin and viridinic acid (?), and, probably, between quercitron tannin and quercitronic acid. The constitution of the tannins hitherto analyzed, may be expressed by the following empirical formulæ:—



\* Several chemists give for tannic acid the formula  $C_{14}H_6O_{10} = C_{28}H_{12}O_{20}$ , and assume that gallic acid is formed by transposition. Therefore tannin must give the same weight as gallic acid; but we never obtain more, at the highest, than 86 per cent. exclusive of acetic acid, which, according to the formula  $C_{14}H_6O_{10}$ , cannot be formed. The quantity of gallic acid which can be obtained from tannic acid, corresponds quite accurately with the above given quantity. I therefore assume also for coffee tannin, the formula  $C_{18}H_8O_9$ , which better agrees with the analytical results, than the formula  $C_{14}H_8O_7$ , especially in the proportion of hydrogen.

Tannin is employed in medicine, and finds an unlimited use in the tannery, in making ink, in dyeing black; morus tannin, and particularly quercitron tannin, are yellow coloring matters. Coffee tannin and bohea tannin are deserving of notice as constituents of coffee and tea.

Use of tannins.

*Catechu Tannin* (Catechu-Tannic Acid):  $C_{18}H_8O_8 = 3HO, C_{18}H_5O_5$ . It is found in *catechu*, or in *Terra japonica*, a vegetable extract, which is procured in the East Indies, by boiling the fruit of the *Areca palm*. The Bengal catechu must come from *Areca catechu*. We extract catechu with ether, and evaporate the etheric solution under the air-pump. A yellow, pure, astringent-tasting, amorphous mass, easily soluble in alcohol and water, soluble also in ether. It precipitates the salts of peroxide of iron, with a grayish-green color; gives, with tartar emetic, no precipitate, and behaves, in other respects, as above mentioned. The combinations, with mineral acids, are soluble in water, and only, in part, precipitable by an excess of the acids. A dilute aqueous solution, exposed to the air, is colored dark red; if the dark fluid be evaporated, there remains a dark-red transparent mass, only in part soluble in water. Tannin, which, like catechu tannin, forms a grayish-green precipitate with the salts of peroxide of iron, is found in *Artemisia vulgaris*, *absinthium*, *Matricaria*, *Verbena off.*, *Urtica dioica*, in the root of *Rathania*, etc.

*Coffee Tannin* (Kaffeic Acid):  $C_{18}H_8O_9 = 3HO, C_{18}H_5O_6$ , or  $2HO, C_{14}H_6O_5$ , is found in the coffee kernel, in the Paraguay tea (the leaf of *Ilex Paraguayensis*), united to caffein, and in the root of *Chiococca racemosa*. The pounded coffee kernels are boiled out with alcohol, afterwards filtered; the filtrate, mixed with twofold volume of water, is precipitated with a solution of sugar of lead, and the obtained precipitate decomposed by hydrosulphuric acid. A gum-like, astringent-tasting, sourish mass, easily soluble in water and alcohol. It dissolves in concentrated sulphuric acid, with blood-red color. If we boil the tannin with potash lye, we obtain an acid which consists of  $C_{12}H_6O_5$ . The salts of the alkalies and alkaline earths absorb oxygen from the air, become green, and are converted into compounds of viridinic acid. In coffee kernels is found a tannin compound which consists of 7.50 potassa, 29.0 of caffein, and 63.5 of tannin.

*Morus Tannin* (Morin-tannic Acid):  $C_{18}H_8O_{10} = 3HO, C_{18}H_5O_6$ . It is found in yellow wood (*Fustic*, *Morus tinctoria*), in common with morinic acid. The deposit, which is found in the middle of the blocks of yellow wood, consists mostly of tannin. This is boiled out with water; during the cooling, the tannin is mostly precipitated as a light yellow powder, consisting of microscopic needles. Tastes sweetish, astringent, slightly soluble in cold water, but easily soluble in warm, as



well as in alcohol, wood-spirit, and ether. Dissolves in concentrated sulphuric acid, with yellow color; if the freshly-prepared solution be diluted with water, the greater part of the tannin is again precipitated. If we let the cold-prepared sulphuric acid solution stand a few days, a brick-red powder is deposited, the *rufimorinic acid*; and, if this be heated, sulphurous acid is evolved, under diffusion of a strong odor, like phenol. By dry distillation, we obtain pyromorin-tannin (pyrocatechuin). Oxidizing acids, as nitric and chloric acid, and chlorine, completely destroy the tannin. With sulphate of protoxide of iron, we obtain, in a solution of tannin, a greenish-black precipitate, and, with tartar emetic, a yellowish-brown one. The dark-yellow solution of tannin, in pure alkalies and in their carbonates, becomes brownish-black in the air. Alum produces, in a solution of tannin, a lemon-colored precipitate; by addition of carbonate of potash and sugar of lead, a yellow one, which is soluble in boiling water, and, during cooling, is deposited as a lemon-colored crystalline powder; this consists of  $4\text{PbO}, 3\text{C}_{18}\text{H}_7\text{O}_9 = 2\text{PbO}, \text{C}_{18}\text{H}_5\text{O}_7 + 2\text{PbO}, 2\text{HO}, \text{C}_{18}\text{H}_5\text{O}_7 + \text{aq}$ . The black salts of peroxide of iron consist of  $\text{Fe}_2\text{O}_3, 3\text{C}_{18}\text{H}_5\text{O}_7$ .

Morus tannin differs from the other tannins in the property of crystallizing, and in its difficult solubility in cold water, as well as in the solubility of its lead salts in boiling water; but, with skins, it forms leather, and, therefore, possesses the most essential property of tannin.

*Quercitron Tannin* is scarcely known. Is found in the bark of *Quercus tinctoria* (Quercitron), in common with quercitronic acid. This tannin precipitates the salts of peroxide of iron, green; it precipitates a solution of glue, and combines with the skins of animals.

*Tannic Acid* (Gall-nut Tannin):  $\text{C}_{18}\text{H}_8\text{O}_{12} = 3\text{HO}, \text{C}_{18}\text{H}_5\text{O}_9$ . It is found in gall-nuts, in green tea, and, probably, in sumach.\* We extract gall-nut powder, with common ether, in a displacement apparatus; thus we obtain two strata, of which the lower is a concentrated solution of tannin in ether; after the evaporation of this in a vacuum, the pure tannin remains behind. Instead of pure ether, we can employ a mixture of ether and alcohol, for extracting. Tannic acid is amorphous, almost colorless, inodorous; tastes in the highest degree astringent; is easily soluble in water, and soluble with difficulty in alcohol and ether; reddens litmus. Pure tannic acid is

\* It has been assumed, until very recently, that all tannins which, like gall-nut tannin, give a brownish-blue precipitate, with salts of peroxide of iron, are identical. Such tannins are found in the entire genus *Quercus*, particularly in the bark of *Quercus robur*, in very many perennial roots, and are generally called oak tannins; but these tannins are said not to give gallic acid, like gall-nut tannin, and, also, by dry distillation, no pyrogallic acid is obtained.

entirely absorbed from its aqueous solution by a piece of cleaned bladder. Toward reagents, it behaves as mentioned above, with the general properties of the tannins. Dilute *mineral acids* precipitate tannic acid from the aqueous solution, by excess of the acids. The combinations of tannin acid, with the *alkalies*, are deposited, if to an alcoholic solution of tannic acid an alcoholic solution of potassa be added cautiously by drops, so that the tannic acid remains in excess. The potassa compound, after being washed with water, is completely white, crystalline, and easily soluble in water, but soon suffers decomposition; it probably consists of  $(2\text{KO}, \text{HO}, \text{C}_{18}\text{H}_5\text{O}_9) + 2(3\text{HO}, \text{C}_{18}\text{H}_5\text{O}_9)$ . If we add a solution of tannin, in drops, to an excess of a solution of *sulphate of peroxide of iron*, there arises no blue color, because the peroxide of iron is reduced completely to protoxide; if we reverse the procedure, we obtain a blackish-blue precipitate, which is said to consist of  $\text{Fe}_2\text{O}_3, 4\text{C}_{18}\text{H}_8\text{O}_{12}$ , but, probably, is tannate of protoxide of iron (ink, black colors). If the compound be boiled with water it becomes colorless, under evolution of carbonic acid. *Acetate of lead* produces, in a solution of tannic acid, a white precipitate:  $2\text{PbO} + \text{C}_{18}\text{H}_5\text{O}_9$ , and *tartar emetic*, a white gelatinous precipitate:  $\text{StO}_3, \text{C}_{18}\text{H}_8\text{O}_{12}$ . Tannic acid forms insoluble compounds with organic bases.

*Kino Tannin* is found in kino, a vegetable ex- Kino tannin.  
tract from *Coccoloba uvifera*. The aqueous decoction of this extract is precipitated by sulphuric acid, the precipitate, after complete washing, is dissolved in boiling water, and decomposed by baryta water. Appears, in pure condition, as a red, transparent, cracked mass, easily soluble in water and alcohol, almost insoluble in ether, and of pure, astringent taste. From the aqueous solution there is deposited, by access of air, a light-red body, not particularly investigated. Mineral acids precipitate this tannin almost completely; it gives a grayish-green precipitate, with salts of peroxide of iron, and none with tartar emetic.

*Cinchona Tannin* (China Tannin), is found, with Cinchona tan-  
nin.  
quinin and cinchonin (cinchona), in the different cinchona barks. We extract the bark with water containing hydrochloric acid, boil the extract with magnesia, dissolve in acetic acid the precipitate—consisting of tannin, quinin, and magnesia—precipitate the tannin with vinegar of lead, and decompose the tannate of lead by hydrosulphuric acid. A mass easily soluble in water, alcohol, and ether, of slightly yellowish color, and pure astringent taste. Under absorption of oxygen, there is deposited from the aqueous solution a red body, the *cinchona red* (Chinaroth). Cinchona tannin behaves to acids like catechu tannin; the salts of peroxide of iron are precipitated grayish-green, and those of tartar emetic, gray.

Bohea tannin.  
Bohea-tannic  
acid.

*Bohea Tannin* (Bohea-Tannic Acid):  $C_{18}H_{10}O_{13} = 3HO, C_{18}H_7O_{10}$ , or  $2HO, C_{14}H_6O_8$ , is found with tannic acid, in very small quantity in tea (the leaves of *Thea Bohea*).

We mix a boiling hot aqueous decoction of tea with a solution of acetate of lead, remove, after 24 hours, the clear solution from the precipitate, and, with ammonia, throw down the bohea-tannate of lead, which consists of  $3PbO + C_{18}H_7O_{10} + 6aq$ . By itself, the bohea tannin is unknown.

Products of the  
decomposition  
of tannins.  
1. Humin-tan-  
nic acids.

As already given above, tannic acid is converted into gallic acid, by the escape of  $C_4H_2O_2$ , and it is very probable that catechuic and morinic acid are, in like manner, formed from the corresponding tannins.

These acids differ essentially from the tannic acids, because they do not precipitate a solution of glue, do not combine with animal skins, and saturate only 2 atoms of base. But they, like the tannic acids, possess the property, in their aqueous solution, owing to the presence, in excess, of pure alkalies, quickly to absorb oxygen, and, at last, to be converted into a dark-colored substance. These acids, which I call humin-tannic acids, consist of:—

Catechuic Acid	$C_{14}H_6O_6$
Morinic	" $C_{14}H_6O_8$
Gallic	" $C_{14}H_6O_{10}$

Likewise arises, probably from coffee tannin, an acid,  $C_{14}H_6O_7$ , which, with the elements of 1 atom HO, forms viridinic acid,  $C_{14}H_7O_8$ .

Catechuic acid.

*Catechuic Acid* (Catechin):  $3HO, C_{14}H_6O_6$ , or  $HO, C_{14}H_6O_6$ ; *anhydrous*,  $C_{14}H_6O_6$ , is found, with catechu tannin, in catechu. We extract these by cold water from the tannin, boil out the residue with water, and, to the hot filtered solution, add a solution of acetate of lead so long as a colored precipitate is formed; filter, and precipitate the catechuic acid from the filtrate by vinegar of lead, quickly wash the yellow catechuate of lead, diffuse the precipitate in water of  $70^\circ$  to  $80^\circ$ , and decompose by hydrosulphuric acid. From the warm filtered solution the catechuic acid separates, during the cooling, in fine white needles, which contain one atom water of crystallization, that escapes at  $100^\circ$ ; tastes bitter, slightly astringent, melts in the heat, dissolves in 1133 parts cold water and 4 parts boiling; easily soluble in cold and warm alcohol; soluble with difficulty in ether. The aqueous solution is easily decomposed in the air. By the presence of carbonate of potassa, the catechuic acid is converted into rubinic and japonic acid, under the absorption of oxygen and formation of carbonic acid. By dry distillation, it gives pyrocatechin (pyromorinic acid). Catechuic acid does not drive carbonic acid from its compounds; the aqueous solution of the



acid produces a blackish-blue color in salts of protoxide of iron, containing some peroxide. Nitrate of protoxide of mercury, chloride of gold, oxide of silver, etc., are reduced by the acid.

*Viridinic Acid*:  $\text{HO}, \text{C}_{14}\text{H}_6\text{O}_7$ . If the aqueous solution of coffee tannin be mixed with excess of ammonia, the dark-yellow fluid assumes, under absorption of oxygen, a bluish-green color, and upon the addition of a solution of acetate of lead, we obtain a blue precipitate of viridinate of lead:  $\text{PbO}, \text{C}_{14}\text{H}_6\text{O}_7$ . By decomposing the lead compound with hydrosulphuric acid, evaporation, etc., an amorphous mass is obtained; easily soluble in water; this mass is dissolved in hydrate of sulphuric acid, with a carmine-red color; if we mix the solution with water, blue flakes are deposited. Viridinic acid.

*Caffeic Acid* is obtained, if coffee kernels, freed from tannin by extraction with alcohol, be boiled out with water, the aqueous extract precipitated with vinegar of lead, and the obtained precipitate decomposed by hydrosulphuric acid. After evaporation of the aqueous solution, there remains a dark-brown extract, which tastes very sour; is very easily soluble in water and alcohol, and by nitrate of peroxide of iron, is colored a beautiful emerald green. Caffeic acid.

*Morinic Acid* (Morin):  $\text{C}_{14}\text{H}_6\text{O}_8 = 2\text{HO}, \text{C}_{14}\text{H}_4\text{O}_6$ . If we let a concentrated decoction of yellow wood stand a few days, we obtain a thick deposit, consisting of morin tannin and morinate of lime. If this, after pressing, be dissolved in boiling alcohol and the solution poured into twice its volume of water, the morinate of lime separates. By boiling the last with alcohol and some oxalic acid, filtering the hot solution, and mixing the filtrate with cold water, we obtain morinic acid as a white, crystalline powder of bitter taste, which becomes yellow in the air. Almost insoluble in water, easily soluble in alcohol and ether. By concentrated sulphuric acid, it is absorbed with yellow color, and with dilute, it is colorless like morin tannin; it gives, with concentrated nitric acid, oxypikrinic acid. Alkalies dissolve morinic acid with yellow color; perchloride of iron produces a garnet-red color, and sulphate of peroxide of iron an olive-green precipitate. A trace of ammonia imparts a yellow color to morinic acid. Morinic acid.

*Rufimorinic Acid*:  $\text{C}_{14}\text{H}_7\text{O}_8$ . From the cold prepared solution of morin tannin in hydrate of sulphuric acid, the rufimorinic acid is deposited, after some time, as a red powder, which is obtained pure by solution in alcohol and precipitation with water. Appears, after drying, as a beautiful red powder; easily soluble in alcohol, soluble with difficulty in water, and scarcely soluble in ether. This powder, by boiling with baryta water, is said to be again converted (how?) into morin tannin. Brought together with the slightest portion of ammonia, rufimorinic acid assumes a splendid carmine-red color. The dark scarlet- Rufimorinic acid.



red, crystalline lead salt consists of  $2\text{PbO}, \text{C}_{14}\text{H}_7\text{O}_8$ . Rufimoric acid is said to be identical with carminic acid (*vide* Coloring Matters.)

*Quercitronic Acid* (Quercitrin):  $\text{HO}, \text{C}_{16}\text{H}_8\text{O}_9$  or  $\text{HO}, \text{C}_{14}\text{H}_7\text{O}_8$ . We extract the bark of *Quercus tinctoria* (Quercitron) with alcohol, remove the tannin by a moistened bladder, distil off the alcohol, dissolve the crystalline crusts deposited in the residue in alcohol, precipitate the coloring matter by water, and purify it by recrystallization from alcohol. Crystalline, sulphur-yellow, inodorous powder; slightly bitter; is dissolved in 400 parts boiling water, and in 4 to 5 parts absolute alcohol. Gives, by dry distillation, pyroquercitrin (?). In the air, the solution assumes a brown color. If we evaporate the alkaline solution, the residue no longer contains quercitronic acid. The hot alcoholic solution gives, with sugar of lead, a beautiful yellow precipitate,  $\text{PbO}, \text{C}_{16}\text{H}_8\text{O}_9$ . Finds employment in the yellow dye.

*Gallic acid.* *Gallic Acid*:  $\text{C}_{14}\text{H}_6\text{O}_{10} = 2\text{HO}, \text{C}_{14}\text{H}_4\text{O}_8 = \bar{\text{G}}$ . Gallic acid is found in many plants with tannin. If we let gall-nut powder, moistened with water, stand a long time, the tannin vanishes, and is also, by exclusion of air, converted into gallic acid by a process of fermentation; gall-nut tannin suffers the same change, if it be boiled a short time, under exclusion of air, with dilute hydrochloric or sulphuric acid, or with a dilute alkali solution; we obtain gallic and acetic acid. If we leave an aqueous solution of tannin, in contact with air, after some time gallic acid is deposited, under absorption of oxygen, and simultaneous production of carbonic acid. A saturated solution of tannin in moderately concentrated potassa solution, exposed to the air in a flat vessel, becomes, by degrees, opaque, under formation of *tannoxylic acid* ( $\text{C}_{15}\text{H}_8\text{O}_{14}$ ?) and carbonic acid, and if the dark-colored fluid be heated to boiling, the tannoxylic acid is converted into gallic acid. Gallic acid is most easily obtained by digestion of gall-nut tannin with dilute hydrochloric acid; treatment with animal charcoal and recrystallization. Crystallizes in long, slightly acid astringent needles; requires 100 parts cold water and 3 parts boiling for solution; easily soluble in alcohol and soluble with difficulty in ether. At  $210$  to  $215^\circ$  it decomposes into pyrogallic and carbonic acid; the aqueous solution soon decomposes in the air under production of mould. It behaves towards oxidizing bodies like the tannins. By concentrated sulphuric acid, it is dissolved with a purple color; if the solution be heated to  $140^\circ$  red crystals of rufingallic acid are precipitated. If we boil gallic acid with acid carbonate of lime, it is thus changed into *gallerythric acid*. Although gallic acid is very weak, it combines with all bases, and gives, in part, crystallizable salts. The alkali salts decompose by excess of base under access of air, become dark colored, and,

under absorption of oxygen, are converted into *tanno-melanic acid salts*. The compounds with the alkalies are obtained in a similar way to the corresponding ones of gall-nut tannin. The potassa salt appears as a white, crystalline, loose powder; easily soluble in water, and  $=2\text{KO}, 3\text{C}_{14}\text{H}_4\text{O}_8 + 6\text{aq}$ . Salts of peroxide of iron are colored dark-blue in the cold by gallic acid; by heating, the color vanishes; a definite compound with iron appears not to exist. Gallates of the alkalies give, with tartar emetic, a white precipitate.

*Tanno-melanic Acid*:  $2\text{HO}, \text{C}_{14}\text{H}_4\text{O}_7$ . If we let a solution of gallic acid in excess of potassa stand, until acetic acid no longer precipitates gallic acid, then oversaturate the whole with acetic acid, and evaporate upon the water-bath, there remains, after extracting the residue with alcohol, a body soluble in water. This body gives, with sugar of lead, a brownish black precipitate, which consists of  $2\text{PbO}, \text{C}_{14}\text{H}_4\text{O}_7$ . Tanno-melanic acid.

*Rufin-gallic Acid* (Para-ellagic Acid, Rubi-gallic Acid):  $\text{C}_{14}\text{H}_4\text{C}_8$ . Production, *vide* Gallic Acid. Shining, almost scarlet-red crystals, which are dissolved in 3000 parts water. From the alkaline solution it is deposited after a time in red crystals easily soluble; salts of peroxide of iron are colored violet. Rufin-gallic acid.

*Ellagic Acid*:  $2\text{HO}, \text{C}_{14}\text{H}_2\text{O}_7$ , is formed with gallic acid by spontaneous decomposition of gall-nut extract; it is found in many benzoin, particularly in those of Coromandel; it is said also to occur in the root of *Tormentilla erecta*. Ellagic acid is insoluble in boiling water, and can, therefore, be separated from gallic acid; from the solution in dilute potassa, it is precipitated by an acid. Slightly yellowish-colored powder; tasteless and inodorous; insoluble in water, alcohol, and ether. If we let the alkaline solution stand in the air, we obtain dark-blue crystals of *glauco-melanoate of potassa*. Ellagic acid.

*Pyrotannic Acids*. The pyrotannic acids arise by heating the humin-tannic acids under simultaneous production of carbonic acid; they contain 2 atoms less carbon than the humin-tannic acids, scarcely possess acid properties, likewise saturate 2 atoms of base, and in the alkaline solution entirely absorb the oxygen from the air under complete decomposition, and can, therefore, be employed in eudiometrical researches. With pyrotannic acid, rubinic and japonic acid agree in constitution. Pyrotannic acids.

*Pyromorin-tannic Acid* (Pyrocatechin):  $2\text{HO}, \text{C}_{12}\text{H}_4\text{O}_2$ , is formed by dry distillation of catechuic acid, of morintannin, and morinic acid. It sublimes similar to benzoic acid in broad, very shining leaflets, and is deposited from the aqueous solution in small, shining, rhombic crystals; tastes bitter, and burning; melts at  $100^\circ$ ; easily soluble in water and

alcohol, and soluble with difficulty in ether; the aqueous solution becomes red in the air and black by the presence of alkalis. Gives no precipitate with a solution of glue, tartar-emetic, and quinin salts. A sugar of lead solution produces a white precipitate, which consists of  $2\text{PbO}, \text{C}_{12}\text{H}_4\text{O}_2$ . Perchloride of iron even in very dilute solution, assumes, upon the addition of pyromorintannic acid, a beautiful green color; ammonia converts the color into violet.

*Rubinic Acid:*  $\text{C}_{12}\text{H}_4\text{O}_6$  or  $\text{C}_{18}\text{H}_6\text{O}_9$ . If a solution of catechuic acid in carbonate of potassa be left to spontaneous evaporation, the residue contains rubinate of potassa. If we mix the solution of rubinate of potassa with hydrochloric acid, the precipitate, after drying, is japonic acid.

*Japonic acid.* *Japonic Acid:*  $\text{HO}, \text{C}_{12}\text{H}_4\text{O}_4$ , appears as a black acid-reacting mass, scarcely soluble in water, which forms with bases dark-colored uncrystalline salts. The anhydrous japonic acid is isomeric with chinon.

*Pyrogallic acid.* *Pyrogallic Acid:*  $\text{C}_{12}\text{H}_6\text{O}_4$ . If gallic acid dried at  $100^\circ$ , be heated in a small retort (best in a chloride-of-zinc bath) to  $210^\circ$ , pyrogallic acid sublimes in white, inodorous, very bitter leaflets; does not react acid; is dissolved in  $3\frac{1}{2}$  parts water; if the solution be evaporated in a vacuum, the acid crystallizes in anhydrous needles. Easily soluble in alcohol and ether; melts at  $115^\circ$ ; sublimes at  $210^\circ$  in colorless vapor, which is slightly suffocating, and excites coughing. A solution in excess of potash-lye becomes dark-colored in the air, under production of acetate, formate, and carbonate of potassa. Oxidizing acids, as well as the halogens, destroy the acid in a moment. The alkali salts are easily soluble in water; the potassa salt crystallizes in white, rhombic tables. The lead salt,  $2\text{PbO}, \text{C}_{12}\text{H}_6\text{O}_6$ , appears as a flocculent, voluminous precipitate.

*Melan-gallic acid.* *Melan-gallic Acid:*  $\text{HO}, \text{C}_{12}\text{H}_3\text{O}_3$ , is formed by heating gall-nut tannin, gallic acid, and pyrogallic acid to  $240^\circ$ . It is precipitated from the alkaline solution by an acid, as a black, shining, tasteless, and inodorous mass, insoluble in water, alcohol, and ether; it expels carbonic acid from the alkali carbonates. The neutral alkali solution gives black precipitates with solutions of the salts of the alkaline earths and of oxides of the heavy metals.

### Second Group.

### LICHEN ACIDS.

Occurrence and general properties of the lichen acids.

To the tannins are directly allied a few weak acids, which are found in different lichens, and are particularly distinguished by easily dividing into new compounds, and, therefore, like the tannins, can



be regarded as constituted of several molecules; they differ from the tannins, by their difficult solubility in water. The compounds of this group, at present known, correspond to the following formulæ:—

Alphaorsellic Acid (Roccellic Acid)	.	$\text{HO}, \text{C}_{16}\text{H}_7\text{O}_7,$
Betaorsellic	" (Roccic Acid)	$\text{HO}, \text{C}_{31}\text{H}_{16}\text{O}_{15},$
Evernic	"	$\text{HO}, \text{C}_{34}\text{H}_{16}\text{O}_{14},$
Gyrophanic	" (Lecanotarie Acid)	$\text{HO}, \text{C}_{36}\text{H}_{18}\text{O}_{15},$
Erythrinic	"	$2\text{HO}, \text{C}_{40}\text{H}_{22}\text{O}_{20},$
Usinic	"	$\text{HO}, \text{C}_{34}\text{H}_{18}\text{O}_{14},$
Chrysophanic	"	$\text{HO}, \text{C}_{40}\text{H}_{16}\text{O}_{16},$
Cetraric	"	$\text{HO}, \text{C}_{34}\text{H}_{16}\text{O}_{15}.$

If we boil alphaorsellic acid with baryta water, it is converted, by absorption of one atom of water, Their decomposition. into orsellinic acid,  $\text{HO}, \text{C}_{16}\text{H}_8\text{O}_8$ , which, by longer boiling, divides into orcin,  $\text{C}_{14}\text{H}_8\text{O}_4$ , and 2 atoms carbonic acid. If we boil betaorsellic acid with water, it divides into orsellinic acid and roccellinin,  $\text{C}_{18}\text{H}_8\text{O}_7$ ; in like manner, evernic acid, by taking up the elements of 2 atoms water, separates into orsellinic acid and evernic acid,  $\text{C}_{18}\text{H}_{10}\text{O}_8$ . Gyrophanic acid decomposes into orsellinic acid and into  $\text{C}_{20}\text{H}_{10}\text{O}_7$ , (?), and 1 atom erythrinic acid, +2HO, are equal to 1 atom orsellinic acid and 1 atom pikroerythrin,  $\text{C}_{24}\text{H}_{16}\text{O}_{14}$ . Usinic, chrysophanic, and cetraric acid give no orsellinic acid. Then the orsellinic acid again divides into carbonic acid and orcin, hence the acids which give orsellinic acid can be expressed by the following formulæ:—

Alphaorsellic Acid	$\text{HO}, \text{C}_2\text{O}_4 \sim \text{C}_{14}\text{H}_8\text{O}_4 +$	$= \text{HO}, \text{C}_{16}\text{H}_8\text{O}_8,$
Betaorsellic	" $\text{HO}, \text{C}_2\text{O}_4 \sim \text{C}_{14}\text{H}_8\text{O}_4 + \text{C}_{18}\text{H}_8\text{O}_7 =$	$\text{HO}, \text{C}_{34}\text{H}_{16}\text{O}_{15},$
Evernic	" $\text{HO}, \text{C}_2\text{O}_4 \sim \text{C}_{14}\text{H}_8\text{O}_4 + \text{C}_{18}\text{H}_8\text{O}_6 =$	$\text{HO}, \text{C}_{34}\text{H}_{16}\text{O}_{14},$
Gyrophanic	" $\text{HO}, \text{C}_2\text{O}_4 \sim \text{C}_{14}\text{H}_8\text{O}_4 + \text{C}_{20}\text{H}_{10}\text{O}_7 =$	$\text{HO}, \text{C}_{36}\text{H}_{18}\text{O}_{15},$
Erythric	" $2\text{HO}, \text{C}_2\text{O}_4 \sim \text{C}_{14}\text{H}_8\text{O}_4 + \text{C}_{24}\text{H}_{14}\text{O}_{12} =$	$2\text{HO}, \text{C}_{40}\text{H}_{22}\text{O}_{20}.$

If orcin be exposed to the common action of ammonia and oxygen, it is converted into a red coloring matter, *orceïnic acid*,  $\text{NC}_{14}\text{H}_7\text{O}_6$ , which forms violet-red compounds, with the alkali bases. Now, 1 atom of orcin is  $\text{C}_{14}\text{H}_8\text{O}_4 + \text{O}_6 + \text{NH}_3 = \text{NC}_{14}\text{H}_7\text{O}_6 + 4\text{HO}$ . The employment in the dyery of lichens, which afford orsellinic acid, depends upon this coloring matter. If it, in a pulverized condition, be exposed to the influence of water, air, and ammonia, the already mentioned division and production of coloring take place by a fermentation process (*vide* under Orseille [orchill] and Litmus).

We obtain the lichen acids from the lichens by boiling the latter with excess of milk of lime, and decomposing the obtained solution by hydrochloric acid. The gelatinous precipitate is dissolved in warm (not boiling) alcohol;

Production of lichen acids.



during the cooling, the acid is deposited, and it is purified by recrystallization and treatment with animal charcoal.

*Alphaorsellic Acid* (Roccellic Acid):  $\text{HO}, \text{C}_{16}\text{H}_7\text{O}_7$ , is found in a South American variety of *Rocella tinctoria*. Colorless crystals, scarcely soluble in water, but easily soluble in alcohol and ether; the alcoholic solution reddens litmus; it gives, with alkalis and alkaline earths, crystallizable salts, easily soluble in water. If a solution of chloride of lime be poured upon the acid, the latter immediately assumes a deep-red color; by degrees, the color vanishes under production of a dark-green, uncrystallizable body. The *Baryta salt* consists of  $\text{BaO}, \text{C}_{16}\text{H}_7\text{O}_7$ .

*Betaorsellic Acid* (Roccic Acid):  $\text{HO}, \text{C}_{34}\text{H}_{16}\text{O}_{16}$ , is found in *Rocella tinctoria*, from Cape of Good Hope. In the production, according to the above-described manner, we obtain a mixture of betaorsellic acid, with roccellin. The separation takes place by warm water, in which betaorsellic acid is rather easily dissolved. In properties, it agrees with alphaorsellic acid, but, by boiling with water and alcohol, it is decomposed into orsellinic acid and roccellin.

*Evernic Acid*:  $\text{HO}, \text{C}_{34}\text{H}_{16}\text{O}_{14}$ , is found in *Evernia prunastri*. Crystallizes, colorless, almost insoluble in cold water, soluble with difficulty in boiling, easily soluble in alcohol and ether, inodorous, and tasteless. Chloride of lime imparts a yellowish color to evernic acid; the solution, in an excess of ammonia, becomes, when exposed to the air, dark-red. If we boil the potassa salt,  $\text{KO}, \text{C}_{34}\text{H}_{16}\text{O}_{14}$ , consisting of silky crystals, with a dilute solution of potassa, we obtain evernic acid, and, by long boiling with baryta water, carbonic acid, and orcin. Since evernic acid furnishes no orcin, it is to be assumed that evernic acid divides into orsellinic and evernic acid.

*Gyrophanic Acid* (Lecanotarie Acid):  $\text{HO}, \text{C}_{36}\text{H}_{18}\text{O}_{15}$ , is found in different species of *gyrophan* and in *Lecanora tartarea*. Forms small soft crystals; colorless and tasteless; insoluble in boiling water, soluble with difficulty in alcohol and ether. A solution of chloride of lime colors the solution red. Gives, after long boiling with alkali bases, orcin and carbonic acid; decomposes, therefore, at first, probably into orsellinic acid and  $\text{C}_{20}\text{H}_{10}\text{O}_7$ .

*Erythric Acid* (Roccifucic Acid, Erythrine):  $2\text{HO}, \text{C}_{40}\text{H}_{22}\text{O}_{20}$ , is found in *Rocella tinctoria* var. *fuciformis*, or *Rocella montagnei*. Crystallizes, colorless, and inodorous; is dissolved in 240 parts boiling water, almost insoluble in cold, easily soluble in alcohol and ether, sharply acid; is colored blood-red by chloride of lime. By boiling with water, it is decomposed into orsellinic acid and pikroerythrin, and by boiling with baryta water, leaves with pikroerythrin, erythrolinic acid, which, however, is probably identical with orsellinic acid. Gives orcin by

dry distillation. Easily soluble in pure alkalies and their carbonates, in lime water and baryta water. Perchloride of iron colors the alcoholic solution purple-red.

*Acid from Lecanora parella* (Lecanoparic Acid). Lecanoparic acid.  
In this lichen an acid is found, which, by boiling with lime, decomposes into orsellinic acid and parellic acid,  $C_{16}H_6O_6$ .

*Orsellinic Acid* (Lecanoric Acid):  $HO, C_{16}H_8O_8$ . Products of decomposition of the lichen acids.  
From its combination with bases, orsellinic acid is precipitated with hydrochloric acid. It crystallizes from water or dilute alcohol in colorless sharply sour and bitter prisms; rather easily soluble in boiling water; a solution of chloride of calcium produces a transient violet color. Becomes deep-red in the air by presence of ammonia. Gives, with baryta, an easily soluble salt.

*Orsellinate of Ethyl* (Erythrin Ether, Lecanora Ether, Pseudoerythrin). Pseudo-erythrin.  
If we boil orsellic, erythric, or alphaorsellinic acid with alcohol, we obtain micaceous, colorless leaflets; easily soluble in boiling water, soluble in alcohol and ether; at first tasteless, but afterwards taste burning. By heating with hydrate of potassa decomposes into alcohol, orcein, and a few other products. The compound of oxide of methyl is procured in the same way.

*Roccellinin*:  $C_{18}H_8O_7$ . Production *vide* Betaorsellinic Acid. Roccellinin.  
White, ciliary, silky crystals; insoluble in boiling water; colored permanently light-green by chloride of calcium; reddens in the air by the presence of ammonia, but gives no orcein by boiling with baryta water.

*Roccellin* (Roccellous Acid):  $HO, C_{24}H_{22}O_5$ , is found Roccellous acid.  
in *Roccella tinctoria*, and is not to be confounded with roccellinin. We obtain roccellous acid, if the lichens are extracted with aqueous ammonia, the solution diluted with water and precipitated by chloride of calcium, and the precipitate decomposed by hydrochloric acid. From the etheric solution it forms fine, silken, tasteless, and inodorous crystals insoluble in water, but soluble in alcohol and ether; melts at  $130^\circ$ , and burns like a fat.

*Pikroerythrin* (Roccinin, Telerythrin?):  $C_{24}H_{16}O_{14}$ . Pikroerythrin.  
Production, see *Erythric Acid*. We neutralize erythric acid with baryta or lime, boil, decompose with hydrochloric acid, filter off the erythrolinic acid, and evaporate the filtrate considerably. After a few days, the pikroerythrin is deposited in crystals and is purified by recrystallization from boiling water. Small, colorless, bitter-tasting needles, united in heaps, which are colored dark-red by the action of ammonia and oxygen, and by a solution of chloride of lime. By continued boiling with water, it suffers scarcely any decomposition, but by boiling with baryta water decomposes into erythroglucin, orcein, and carbonic acid; gives, by heating, orcein.

*Erythroglucin*. *Erythroglucin* (Rocceglucin, Pseudo-orcin, Erythromannit):  $C_{22}H_{28}O_{22}(?)$ , forms colorless, neutral, sweet-tasting crystals, often an inch long, of a diamond lustre; soluble in water and alcohol; quite indifferent; is not changed by chloride of lime, and, with nitric acid, gives nitroerythroglucin, a violently exploding nitrogen compound  $= C_{22}H_{18}O_{12}, 10NO_4(?)$ .

*Everninic acid*. *Everninic Acid*:  $C_{18}H_{10}O_8$ . We let evernic acid, with a pure solution of potassa in excess, boil a few minutes, neutralize the dark-brown fluid with carbonic acid, evaporate, and by hydrochloric acid decompose the everninate of potassa, which, after some time, separates. Produces, from the hot aqueous solution, long, capillary, silky, inodorous, and tasteless crystals; slightly soluble in cold water; easily soluble in boiling, as well as in ether and alcohol. Is colored yellow by a solution of chloride of lime; gives no orcin. The baryta salt,  $BaO, C_{18}H_9O_7$ , crystallizes in fan-shaped groups of prisms. *Everninate of ethyl* is tasteless and inodorous; insoluble in water, soluble in alcohol and ether; melts at  $56^\circ$ .

*Orcin*. *Orcin* (Roccin):  $C_{14}H_8O_4 + 2aq$ , is obtained quite pure by long boiling orsellinic acid with water, as well as by dry distillation of lichen acids. We obtain orcin directly from lichens by extracting the latter with lime and water, and long boiling the obtained extract; we afterwards precipitate the lime by carbonic acid, evaporate and dissolve the residue with boiling alcohol. Or, we boil the lichens with alcohol. Crystallizes in colorless prisms; easily soluble in water and alcohol; tastes aromatically sweet; melts, and may be sublimed unchanged. Nitric acid colors orcin, at first, blood-red, and later complete decomposition takes place. With bromine we obtain  $C_{14}H_5Br_3O_4$ . A solution of chloride of lime colors it violet; gives, with oxide of lead, a compound  $= 5PbO, C_{14}H_8O_4$ .

*Orcein*. *Orcein* (Roccein, Orceic Acid):  $NC_{14}H_7O_6$ . We let moistened finely-ground orcin stand under a bell glass with aqueous ammonia, until a dark fluid is formed, dilute with water, to which a few drops of ammonia have been added, and precipitate the orcein from the reddish violet solution by acetic acid. A dark-brown powder; gives, with ammonia, a deep-red solution, and with fixed alkalies a violet one, which is bleached by hydrosulphuric acid, without deposition of sulphur; acids again restore the red color under evolution of hydrosulphuric acid. With nitrate of silver the ammonia solution gives a dark violet precipitate  $= 2AgO + NC_{14}H_7O_6(?)$ .\*

#### \*ORCHILL AND LITMUS.

Under *Orchille* (Archil, Orseille), *persio*, and *cudbear* is understood a pasty mass, which occurs in commerce as a coloring matter, and is procured from the above-mentioned lichens. For this purpose are used particularly *Lichen roccellus*, *Variolaria dealbata*, *Gyrophora pustulata*, etc.



*Usnic Acid*:  $C_{34}H_{18}O_{14}$ . A body, widely diffused in lichens; is found in the species *Usnea* (*Usnea florida*, *hirta*, *plicata*, *barbata*), *Parmelia*, probably in all species of *Cladonia*, *Lecanora*, etc. Forms, from the etheric solution, sulphur-yellow, brittle, prismatic crystals; insoluble in water, soluble with difficulty in alcohol and ether; melts at  $200^{\circ}$ , like a resin; sublimes, in part, unchanged under evolution

2. Lichen acids, which contain no orsellinic acid, and, therefore, also give no orcein.

Usnic acid.

The lichen powder is made into a paste with urine, and in a warm room, with access of air, left to fermentation. After five or six weeks the formation of pigment is terminated. The urea of the urine furnishes ammonia, which, in common with the oxygen of the air, acts upon lichen acids, whereby the latter are converted into coloring matters. One would conjecture that the coloring matter present in orchill must be orcein; but the researches before us have never rendered that conjecture satisfactory; they, however, require repetition. According to them, orchill contains two coloring matters, the alphaorcein and betaorcein, which neither in constitution nor in physical relations agree with orcein; thus alphaorcein consists of  $NC_{18}H_{10}O_5$ , and betaorcein of  $NC_{18}H_{10}O_8$ ; both possess a beautiful red color, are only slightly soluble in water, but are rather easily soluble in alcohol with a red color. By salts they are completely precipitated from the aqueous solution. By oxidation, alphaorcein appears to be converted into betaorcein.

They dissolve in alkali fluids with beautiful purple color; if we saturate the solution with common salt, we obtain precipitates, which consist of the alkalis and the coloring matters. If we conduct hydro-sulphuric acid into an alkali solution of these matters, the solution is bleached without deposition of sulphur; by heating, the solution again assumes its former color under evolution of  $H_2S$ . The same follows, if hydrogen, at the moment of its liberation, comes in contact with the coloring matter; in the air the colorless fluid again assumes the red color. A solution of the coloring matter in ammonia gives differently colored precipitates with the oxides of the heavy metals. Perhaps these coloring matters are paired compounds of orcein with hydrocarbons. Orchill finds employment in dyeing, but the coloring matters are not durable.

*Litmus* (Tournesol) is procured principally from *Lecanora tartarea*. The ground lichens, mixed with alkaline ammonia fluid, are left to putrefaction, and after four or five weeks a measure of alum, potash, and lime is added, under whose influence the particular litmus matters are formed. When the maximum of these is reached, the pasty mass is mixed with sand, formed into cubes and dried. The essential coloring matter of litmus is said to be azolitmin,  $NC_{18}H_{10}O_{10}$ , and is formed by oxidation of betaorcein. Azolitmin.

Azolitmin is a dark-red, uncrystalline powder; slightly soluble in water, with a red color. This substance unites with alkalis, forming blue compounds, whereby the litmus coloring matter essentially differs from the coloring matters of orchill (employment of litmus as reagent upon acids and alkalis). In other respects, azolitmin behaves quite like alphaorcein and betaorcein. Besides azolitmin, litmus is said to contain other coloring matters; particularly, 1st. *Azoerythrin*,  $NC_{22}H_{19}O_{22}$ , a body insoluble in water, alcohol, and ether; soluble in alkali fluids, with wine-red color; gives brownish-red compounds with oxides of metals; by escape of carbonic acid, azoerythrin is said to be converted into alphaorcein and betaorcein. 2d. *Erythrolein*,  $C_{26}H_{22}O_4$ , and 3d. *Erythroleinic acid*,  $C_{26}H_{22}O_8$ , which dissolve in water, alcohol, and ammonia, with beautiful red color; and also is found, in small quantity, in orchill. 4th. *Erythrolitmin*,  $C_{26}H_{22}O_{12}$ , is said to be the principal constituent of litmus besides azolitmin; is dissolved in alcohol, and is deposited from the hot saturated solution in dark-red crystals. This coloring matter is said to arise from the above-mentioned roccellous acid, which, however, is not probable. 5th. *Spaniolitmin*,  $C_{26}H_{11}O_{23}$ , is said to occur sometimes in litmus, and form blue compounds with alkalis. Spaniolitmin.

Azoerythrin, wine-red pigment.

Erythrolein and erythroleinic acid.

Erythrolitmin.



of a vapor, violently attacking the organs of respiration, and the simultaneous production of *betaorcine*. It easily dissolves in pure alkalies; if the solution be exposed to the air, it assumes, after a little time, a dark-red color; acetic acid then produces a golden-yellow precipitate; soluble in alcohol. Usnic acid is dissolved with a yellow color by concentrated sulphuric acid, and again precipitated upon the addition of water. The combinations with alkalies are colorless; crystallizable; soluble with difficulty in water, easily in alcohol; the compounds, with the earths and oxides of heavy metals, are insoluble.

*Betaorcine*. *Betaorcine* (Betaroccin):  $C_{34}H_{18}O_6(?)$ . Forms colorless prisms, dissolves in water with more difficulty than orcein, easily soluble in alcohol and ether, volatile; assumes, in contact with air and ammonia, after a few minutes, a red color, and, under the influence of pure alkalies and their carbonates, is converted into a beautiful red coloring matter. Is colored red by a trace of the chloride of calcium solution.

*Rhabarberic acid*. *Chrysophanic Acid* (Rhabarberic Acid, *Rhein*, *Parietin*):  $HO, C_{40}H_{16}O_{16}(?)$ , is found in *Lichen parietinus*, and in rhubarb root (*Rheum palmatum*, *compactum*, and *undulatum*). Is often obtained from *Lichen parietinus*, in the manner above given. From the rhubarb root it can be extracted by ether; the crystals, which are deposited from the solution, are purified by recrystallization from alcohol. Appears in stelliform groups of golden needles, having a metallic lustre; tasteless, and inodorous, almost insoluble in cold water and alcohol, rather easily in ether, with a reddish-yellow color; sublimes partly undecomposed; is dissolved without suffering change in concentrated sulphuric acid, likewise in cold concentrated nitric acid; but if the solution be warmed, it forms a red substance, soluble in ammonia, with a splendid violet color. The ammonia solution suffers no change of color from acetic acid. Chrysophanic acid gives, with alkalies, deep red solutions; the salts are immediately decomposed by carbonic acid. Rhubarb root contains still other uncrystallizable resins, *Erythroretin*:  $C_{16}H_9O_7$ , and *Phanoretin*:  $C_{18}H_8O_7$ , which, in contact with alkalies, are colored splendid red. By internal use of rhubarb, these bodies pass into the urine, which can immediately be known if we make the urine alkaline.

*Cetrarin*. *Cetrarin* (Cetraric Acid):  $C_{34}H_{16}O_{15}$ , is found in Iceland moss (*Cetraria Islandica*). We boil the lichen with strong alcohol and some carbonate of potassa, and decompose the boiling hot extract with hydrochloric acid. From the formed precipitate, lichen-stearic acid and lichen-green are absorbed by treatment with weak alcohol, petroleum, and ether. Crystallizes from the alcoholic solution in bitter, colorless, shining

capillary prisms, scarcely soluble in water, but easily in boiling alcohol; expels carbonic acid, and gives very bitter compounds, with alkalies. Easily dissolves in ammonia, with bright yellow color; in the air, the solution becomes brown, and then no longer tastes bitter. Concentrated sulphuric acid colors cetrarin first yellow, then red; hydrochloric acid imparts to it a blue color, and, by concentrated nitric acid, it is converted into a yellow resin.

Substances which, in many respects, are allied to the lichen acids, are found in madder-red, in the root-bark of many trees, and in the leaf-texture of many plants, as in different species of *indigofera*, *Isatis*, etc. Thus, madder contains a yellow, crystallizable body—rubian, which, under the influence of acids, decomposes into sugar, and the true coloring matter—alizarin. *Phloridzin*, which occurs in the root-bark of trees, is converted, like orcein, under the action of ammonia and oxygen, into a beautiful red coloring matter, phloridzein; but it is divided, in contact with acids, into phloretin and sugar, and ranks, in this respect, with salicin. In the different plants from which *indigo* is procured, it does not occur as such, but is first formed by the action of oxygen upon a colorless body, quite in the same manner as the colorless orcein in the air, goes again into colored orcein. I describe indigo as an appendix to the coloring matters which arise from lichen acids; phloridzin is treated in connection with salicin, and the coloring matters of madder are described in the following division.

## INDIGO.

*Indigo* (crude indigo), a coloring matter, distinguished for its durability, is obtained, as above mentioned, from the leaves of many plants, by access of air. The substance, which is converted into coloring matter by oxidation, is found in very different plants; thus, in many species of *Indigofera*, *Galega tinctoria*, *Nerium tinctorium*, *Polygonum tinctorium*, *Asclepias tingens*, in the stalks of many species of *Orchis*, etc. The original substance from which indigo arises is not yet known; probably, however, the fresh plants contain a colorless substance which is soluble in water and alkaline fluids, and, by absorption of oxygen, furnishes indigo (Indigo-white?). Indigo is obtained, if the blooming indigo plant, particularly *Nerium tinctorium*, in a large vessel, be poured over with water of 25°; after a short time fermentation commences, carbonic acid and hydrogen are evolved, whilst a yellow solution is formed, from which, upon the addition of lime water, in contact with air, the indigo is deposited. The indigo occurring in commerce, possesses a dark-blue color, slightly conchoidal fracture, and ground, with a

Crude indigo.  
Its production.

hard body, assumes a copper lustre; insoluble in water, alcohol, and ether, in dilute acids (except nitric acid), and in alkalies.

Constituents of crude indigo. Crude indigo is a mixture of the pure blue coloring matter (highest 45 per cent.) with indigo-gluten, indigo-brown, indigo-red, and earthy substances.

Indigo-brown. *Indigo-brown.* After the indigo-gluten, which belongs to the protein substances, is extracted by dilute acids, the residue is treated with a concentrated solution of potassa, and the indigo-brown precipitated from the alkali solution by an acid. A brown body, almost tasteless, scarcely soluble in water; gives, by dry distillation, nitrogenous products, saturates the alkalies completely, and, with them, gives dark brown combinations, soluble in water.

Indigo-red. *Indigo-red.* The indigo remaining behind after treatment with potassa solution, is boiled a long time with alcohol, in which the indigo-red is dissolved. After evaporation of the alcoholic solution, the indigo-red remains as a blackish brown powder, insoluble in water, alkalies, and acids; in slight quantity, soluble in alcohol and ether, with deep red color; gives, by dry distillation, a snow-white sublimate.

Indigo-blue. *Indigo-blue:*  $\text{NC}_{16}\text{H}_5\text{O}_2$ ,\* is the essential constituent of crude indigo. It possesses the property, as soon as it separates, of forming, with hydrogen, a combination which is soluble in alkalies, and, in contact with oxygen, again furnishes indigo-blue. Hereupon is founded the production of pure indigo-blue. The crude indigo, extracted with hydrochloric acid, dilute potassa, and alcohol, is, in a finely pulverized state, intimately mixed with twofold weight of freshly slaked lime; the mixture is brought into a bottle containing 150 times the weight of indigo, and this is filled with hot water, in which sulphate of protoxide of iron, equal to 4-5th the weight of indigo, has been previously dissolved. The bottle is well stopped, the mass, thoroughly stirred round, is left a long time at rest. Afterwards, the clear yellow fluid, which contains a combination of lime with indigo-white (indigo vat), is drawn off, mixed with some hydrochloric acid, and left in contact with the air until the indigo-blue is completely separated. Or, we mix equal quantities of indigo and grape sugar with hot ordinary alcohol, add strong soda lye, equal to  $1\frac{1}{2}$  times the weight of indigo, stir, and after a few hours, draw off the red solution. Can also be procured by sublimation of crude indigo. The sublimed indigo-blue forms four and six sided prisms; the precipitated appears as a deep blue powder, sometimes amorphous, and sometimes crystalline; tasteless, and inodorous,

\* It is already stated in the General Part, that Indigo-blue stands in a certain relation to the salicyl series, and is easily converted into it,  $\text{NC}_{16}\text{H}_5\text{O}_2 = \text{C}_{14}\text{H}_5\text{O}_2 + \text{NC}_2$ . This constitution is to be considered in the decomposition of indigo.



completely indifferent, insoluble in water, alcohol, ether, dilute acids, and alkalies; sp. gr. 1.31; sublimes completely under diffusion of purple red vapors. If indigo-blue be treated with *oxidizing bodies*, it is converted into *Isatin*,  $\text{NC}_{16}\text{H}_5\text{O}_4$ , and, by the action of concentrated nitric acid, into *nitrosalicylic* and *pikrin-nitric acid*. By the action of *chlorine* and *bromine*, we obtain substitution products of isatin, and, later, derived radicals of *salicyl*. Concentrated boiling *potash lye* decomposes indigo-blue, under production of *chrysanilic* and *anthranilic acid*, and, by heating with hydrate of potash, we obtain *salicylic acid*.

Concentrated, particularly fuming *sulphuric acid*, dissolves indigo-blue with ease; thereby is formed two paired acids, the purple-sulphuric and indigo-blue-sulphuric acid.

Indigo-blue-sulphuric acids.

*Purpur-sulphuric Acid* (Sulphopurpuric Acid):  $\text{HO}(2\text{NC}_{16}\text{H}_5\text{O}_2 + \text{SO}_3)\text{SO}_3 = \text{HO}, \text{N}_2\text{C}_{32}\text{H}_{10}\text{O}_4 + 2\text{SO}_3$ , is obtained, if finely rubbed indigo-blue be shaken in a bottle with 7 to 8 parts English sulphuric acid, until the mixture assumes a green color, when we dilute the mixture with much water. A precipitate is formed which consists of unchanged indigo and purpur-sulphuric acid, and, in the blue solution, are found free sulphuric acid, and also indigo-blue-sulphuric acid. The precipitate is washed out with pure water, upon a filter; if the free sulphuric acid be removed, the purpur-sulphuric acid dissolves, and, after evaporation of the aqueous solution, appears as a solid, dark blue mass, completely soluble in water and alcohol, with a blue color. Acids precipitate it completely from the solution. If, to the aqueous solution, we add any salt, thus is precipitated the purple-sulphate, whilst the acid of the salt remains in the solution. The acid, as well as the salt, is bleached if it comes in contact with hydrogen at the moment of its liberation, and acquires the color again by access of oxygen.

1. Purpur-sulphuric acid.

*Indigo-blue-sulphuric Acid* (Hyposulphindigotic Acid, Cörolin-sulphuric Acid, Soluble Indigo-blue):  $\text{HO}(\text{NC}_{16}\text{H}_4\text{O}_2, \text{SO}_2)\text{SO}_3$ . This acid is formed when sulphuric acid acts upon purpur-sulphuric acid, as well as by long treatment of indigo-blue with sulphuric acid. If indigo-blue-sulphuric acid, diluted with water, be digested with sulphuric acid and perfectly cleansed animal wool, the first is absorbed by the wool, and if the blue wool, washed with water, be treated with carbonate of ammonia, we obtain a solution of indigo-blue-sulphate of ammonia. This is precipitated by acetate of lead, the precipitate, diffused in water, is decomposed by hydrosulphuric acid, and then by evaporation of the colorless solution in the air, the pure acid is obtained. A blackish blue solid mass, of strong acid taste, and soluble in water and alcohol with beautiful blue color. Sunlight, heat, nitric acid, and alkalies decompose indigo-

2. Indigo-blue-sulphuric acid.



blue-sulphuric acid, under formation of *Viridin-sulphuric*, *Purpurin-sulphuric*, *Flavin-sulphuric Acid*, etc., which can also be considered different modifications of indigo-blue-sulphuric acid. Toward hydrogen these acids behave like the preceding. The *indigo-blue-sulphates* are red in transmitted light; those of the alkalies are soluble in water, with beautiful blue color, but insoluble in salt solutions. The *indigo-blue-sulphate* precipitated by sulphate of potassa, is the so-called *Indigo-carmin*, which combines with animal wool, like the pure acid. Indigo-blue-sulphuric acid serves for dyeing wool, which behaves towards the acid like a base.

Indigo-white. *Indigo-white* (Indigin, reduced Indigo):  $\text{NC}_{16}\text{H}_6\text{O}_2 = \text{NC}_{16}\text{H}_5\text{O}_2 + \text{H} = \text{NC}_{16}\text{H}_5\text{O} + \text{HO}$ . If the above (see *Production of Pure Indigo*) mentioned indigo vat be mixed with an acid under complete exclusion of air, a white flocculent precipitate of indigo-white is produced, which is best dried in a current of hydrogen gas. Greenish-white, crystalline, silky, inodorous, and tasteless; insoluble in water, soluble in ether and alcohol; not volatile; divides by heating into water and indigo-blue, under partial decomposition. Absorbs oxygen with great avidity, and is again converted into indigo-blue. Indigo-white behaves towards bases like an acid; if the combination be exposed to the air, indigo-blue is formed under separation of the base. (Employment of indigo-white in the dyery; vats (kuppen), different kinds in use.)

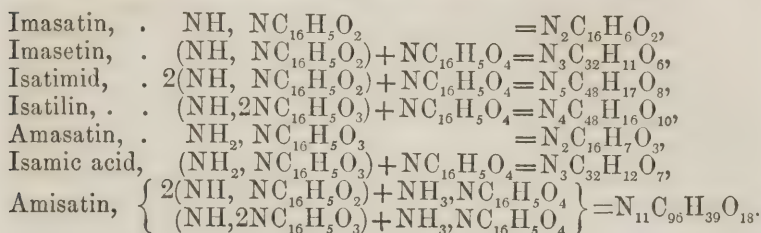
Isatin. *Isatin*:  $\text{NC}_{16}\text{H}_5\text{O}_4$ . This body is formed by oxidation of indigo-blue with chromic acid and dilute nitric acid under co-operation of heat. If the blue color has vanished, the crude product obtained is dissolved in potassa, and the dilute solution cautiously mixed with hydrochloric acid so long as a brown precipitate is formed; afterwards it is filtered, and, by more hydrochloric acid, the isatin is precipitated. Crystallizes from the alcoholic solution in rosy, very shining prisms; dissolves in water with dark-red color; scarcely volatile. Reducing substances do not convert it into indigo-blue. By the action of *chlorine* and *bromine* derived combinations are formed. From the warm solution in sulphide of ammonium is deposited

Isatyd. by cooling, *Isatyd*,  $\text{NC}_{16}\text{H}_5\text{O}_4 + \text{H}$ , which relates to isatin as the indigo-blue to indigo-white. If hydrosulphuric acid be conducted into a solution of isatin, thus we have upon the decomposition of water, *sulphisatin* or *isatin*, in which

Sulphisitin.  $\text{O}_2$  are substituted by  $\text{S}_2 = \text{NC}_{16}\text{H}_5 \left\{ \begin{array}{l} \text{O}_2 \\ \text{S}_2 \end{array} \right.$ . *Sulphurous acid* forms, under co-operation of strong bases, *isatin-sulphuric acid*,  $\text{NC}_{16}\text{H}_5\text{O}_4 + 2\text{SO}_2$ . By the action of *ammonia* upon isatin, a series of compounds is formed, consisting

of imid and amid with reduced isatin, as *imasitin*, *imasetin*, *amasatin*, *isatimid*, *isatilin*, and *amisatin*, corresponding to the following formulæ:—

Amid and imid compounds of isatin.



*Potash-lye* dissolves isatin with dark-red color; from the solution hydrochloric acid precipitates isatin unchanged. But if the solution be heated, it becomes light-yellow, and now contains *isatinat* of potassa,  $\text{KO, NC}_{16}\text{H}_6\text{O}_5$ .

Isitinate of potassa.

If we let potassa act upon *sulphisatin*, we obtain *sulphisatyd*,  $\text{NC}_{16}\text{H}_6\text{O}_3\text{S}$ , and, by the action of bisulphate of ammonia is formed *isaten*,  $\text{NC}_{16}\text{H}_6\text{O}_3$ .

Sulphisatyd.

Isaten.

*Indin*:  $\text{NC}_{16}\text{H}_6\text{O}_2$ , is formed by treating isatyd with potassa. If 2 atoms of indin take the elements of 1 atom water, we have *hydrindin*,  $\text{N}_2\text{C}_{32}\text{H}_{13}\text{O}_5$ , etc. (*compare* "Chemie der organischen Verbindungen," I. p. 986).

Indin.

*Chlorisatin*:  $\text{NC}_{16}\text{H}_3\text{ClO}_4$ , and *Bichlorisatin* (Bichloride of Isatin):  $\text{NC}_{16}\text{H}_3\text{Cl}_2\text{O}_4$ , are formed by the action of *chlorine* upon indigo-blue, indigo-white, and isatin. From the hot saturated solution of both, the chloride of isatin first crystallizes, and then the bichloride of isatin. These bodies quite agree in their chemical and physical relations with isatin, and, brought together with the different reagents, give the corresponding products. The same holds good for *bromide* and *bibromide* of *isatin*.

Chlorisatin and bromisatin.

### Third Group.

#### COLORING MATTERS.

Although the lichen matters and the substances which furnish indigo-blue, are not colored, they can, however, be classed as coloring matters, so far as they possess the property under certain conditions of being converted into them. The same is true for the tannins, a part of which appear as such alone, and part enter as colored compounds, which are employed in the dyery. There are, therefore, in this group, those organic compounds to be described, which occur in nature already in a colored state. It is, however, probable that many of these colored substances arise from those

Some general relations of coloring matters.

originally colorless, by a process of oxidation. Coloring matters are almost exclusively found in the vegetable kingdom (the coloring matter of the blood, "hematin," is mentioned with the protein combinations); many crystallize; they possess, like the tannins, weak acid properties, and unite with oxides of metals and, likewise, with basic salts; forming mostly colored, insoluble combinations (lakes). In their aqueous solution, particularly with excess of alkaline bases, they suffer, under absorption of oxygen, similar decompositions to the tannins, and it is not improbable that many coloring matters stand in a similar relation to particular tannins, as morinic acid to morin tannin. Notwithstanding that the coloring matters, in their physical and chemical properties, particularly in their behavior to the common solvents (resinous, gummy coloring matters, etc.) differ widely from one another; they yet possess a few common characteristics, therefore they can be considered a distinct group of organic substances. These common characteristics distinguish them in their behavior: 1, to *deoxidizing bodies*; 2, to *sulphurous acid*, as well as to *chlorine* and *bromine*, and 3, to *sunlight* under co-operation of atmospheric oxygen.

Behavior to reducing agents.

As indigo-blue, and the coloring matters which arise from lichen acids, form, with *hydrogen*, colorless compounds, which, by access of air, are again converted into the colored state, in like manner, *e. g.*, the coloring matters in Campeachian and Brazilian wood, and in the red beet, etc., are bleached under deposition of sulphur, if they come in contact with hydrosulphuric acid. Many coloring matters, particularly the yellow, suffer no alteration, if they be

Behavior to sulphurous acid.

brought in contact with *sulphurous acid*; others, on the contrary, are bleached, inasmuch as they combine with sulphurous acid, forming colorless compounds. With these may be classed especially the red and the blue flower coloring matters; strong acids, likewise a high temperature, expel the sulphurous acid from them, whereby their former color is restored. In many cases, however, by the action of sulphurous acid, in the presence of oxygen, the coloring matter is changed in such a manner that the former color can no longer be recalled. If we shake a solution of indigo-blue-sulphuric acid with sulphurous acid in the air, it is thus very soon completely bleached under formation of sulphuric acid, and, in contact with oxygen, the color is not again restored. The oxygen which is necessary to the formation of sulphuric acid, is not absorbed from the coloring matter, for the bleaching depends upon its oxidation; in the very moment, for example, in which the oxygen unites with  $\text{SO}_2$  to form  $\text{SO}_3$ , another part of oxygen unites with the coloring matter. If all the sulphurous acid be changed into sulphuric acid, the action of oxygen upon the coloring matter ceases. All substances, which are easily oxidized, as phosphorus, etc., generally act like



sulphurous acid. Alizarin, and the yellow coloring matter of silk, behave to sulphurous acid like indigo-blue. Often, however, the bleaching, by means of this substance, appears to occur in such a manner that water is decomposed, and whilst the oxygen with  $\text{SO}_2$  forms  $\text{SO}_3$ , the hydrogen combines with the coloring matter, and forms with it a colorless compound; then often the color returns, if the yellow matter be brought a few moments into an atmosphere of chlorine. *Chlorine* destroys the color completely (chlorine bleaching, quick bleaching), because it in part indirectly oxidizes and in part forms chlorine compounds by substitution. Like chlorine, direct sunlight appears to destroy all coloring matters, in the presence of oxygen, because, under the influence of light, oxygen is certain to act upon organic matters in the same manner as under the influence of sulphurous acid (turf bleaching). Many coloring matters have a great tendency to combine with the organic fibre. Completely bleached stuffs absorb coloring matters from their solutions, and acquire thereby a more or less durable color. The color is always the more durable, the greater the mutual attraction is, the more the coloring matter resists the action of ordinary agents, and the less it is soluble in water, dilute acids, and alkalies (substantive colors). As already stated, coloring matters have the property of forming insoluble combinations with many basic salts. Therefore, if the attraction of the stuffs for coloring matter be inconsiderable, it can be increased by impregnating with basic salts (mordants) the stuffs to be dyed, and then dipping the latter in the coloring solution. The basic salt imbibes the coloring matter and determines, of course, the coloring of the stuff (adjective colors). Moreover, coloring matters suffer change of color, if they come in contact with acids, alkaline substances, etc., so that one and the same coloring matter often is employed to produce different colors (employment in the art of dyeing). A description follows of only the most important and more accurately known coloring matters.

Behavior to chlorine.

Behavior to sunlight.

Substantive and adjective coloring matters.

*Chlorophyll* (Leaf-green):  $\text{NC}_{18}\text{H}_9\text{O}_8$ . The grasses and leaves of trees owe their green color to chlorophyl. We digest the bruised fresh leaves repeatedly with ether, evaporate the extract upon the water-bath, extract the residue completely with absolute alcohol, evaporate again, and treat the residue with concentrated hydrochloric acid; from the green hydrochloric acid solution the chlorophyl is precipitated by water. Appears, after drying, as a dark-green powder; melts at  $200^\circ$ ; insoluble in water, slightly soluble, with green color, in alcohol, ether, fatty and volatile oils. The etheric solution in the air becomes yellow. If we bring some zinc into the green hydrochloric acid solution, bleaching takes place; by evaporation in the air, the

Chlorophyl.



color again appears; if we bring a piece of marble into the green hydrochloric acid solution, the chlorophyl is thus completely precipitated. It dissolves in concentrated sulphuric acid with splendid green color; also is it in moist condition absorbed by pure alkalies, and their carbonates with green color; with lime water and baryta water, likewise with acetate of lead, chlorophyl gives green precipitates. Leaves contain only a very small quantity of chlorophyl (for its physiological importance, see General Part).

*Xanthophyl* (Leaf-yellow). It is well known that many leaves assume a yellow color in autumn; this yellow color arises, without doubt, from chlorophyl. It appears as a dark-yellow fat; insoluble in water, little soluble in alcohol; dissolves readily in ether. In the sunlight it is completely bleached; soluble in pure alkalies with yellow color.

*Erythrophyl* (Leaf-red, Berry-red). All trees and shrubs, whose foliage becomes red in autumn, bear red fruit. (*Sorbus aucuparia*, *Prunus cerasus*, etc.) Leaf-red is an extractive red coloring matter; easily soluble in water and alcohol; in the air, it is converted into a brown body, soluble with difficulty; gives, with all bases, beautiful grass-green combinations; acids reproduce the red color.

The colors of flowers are, as yet, but little investigated, and, on account of their instability, they are of no importance to the dyery. From the flower-leaves we can extract the coloring matter by alcohol of 80 per cent.; after evaporation, this matter remains like an extract. The coloring matter of blue flowers is blue, violet, or reddish; some zinc, brought into the sour solution, produces bleaching; it dissolves in water or aqueous alcohol, and is insoluble in absolute alcohol and ether. The coloring matter of yellow flowers is rather durable, resinous; mostly insoluble in water, and is colored dark-blue by sulphuric acid. From the blossoms of *Narcissus tacetta*, it is said, a crystallizable and sublimable coloring matter is procured by extraction with ether. The flowers of *Papaver rhæas*, extracted with carbonate of soda, give a red solution; pure potassa colors it green; hydrochloric acid light-red. Red rose-leaves are colored green by alkalies, dark-red by acids, etc.

*Madder root* (*Rubia tinctorum*) is extensively employed in the Turkish-red dyeries on account of its coloring matter, and has been the subject of many investigations, which, however, widely differ from one another. According to the newest work upon madder, its essential constituent appears to be a yellow crystalline body, *rubian*, which, under the influence of acids, decomposes into sugar and the true coloring matter alizarin; the same separation follows also without doubt, in part, in the living root. If the madder be extracted with hot water, and the decoction mixed with an

acid, a dark-brown precipitate is thus formed, which consists of two coloring matters, alizarin and purpurin; of several resins, pectic acid, etc.\* If this precipitate be boiled out with alcohol and the filtered solution mixed with freshly precipitated hydrate of alumina, thus are the coloring matters completely precipitated. A boiling solution of carbonate of potassa withdraws purpurin from this deposit, whilst a compound of alizarin with alumina remains behind, which is decomposed by boiling with hydrochloric acid; alizarin is separated as a red powder. If we let madder ferment, the alizarin vanishes; only purpurin is then present; probably alizarin decomposes into purpurin under separation of carbonic acid and hydrogen.

*Alizarin* (Lizarinic Acid). Anhydrous:  $C_{20}H_6O_6$ : 1. Alizarin. aqueous:  $C_{20}H_6O_6 + 4HO$ . Aqueous alizarin crystallizes in scales resembling mosaic gold; the anhydrous appears in red crystals, which have a spot of yellow. It is soluble in boiling water and cold alcohol, with yellow color; the slightest trace of alkali colors the solution red. The solution in *pure potassa* and *soda*, in concentrated condition, is purple-red by transmitted light, and blue by reflected; the solution in *ammonia* and in *carbonate of the alkalis* is red. Acids separate alizarin in deep orange-colored flakes. *Chloride of barium* and of *calcium* cause in the ammonia solution a purple precipitate; in dry condition almost black  $= 3(BaO, HO) + 2(C_{20}H_6O_6)$  and  $3(CaO, HO) + 2(C_{20}H_6O_6)$ . If we add acetate of lead to the alcoholic solution of alizarin, we thus obtain a deep-red precipitate. *Alumina* bleaches the alkali solution of alizarin, forming a reddish-purple precipitate, and *peroxide of iron* a dark purple one. A solution of *alum* takes up no alizarin in the cold. *Chloride of lime* colors alizarin, suspended in water, yellow. *Sulphuric acid* dissolves it with dark yellowish brown color; even by heating the solution, the alizarin suffers no decomposition. Sulphurous acid has no influence upon the same. Dilute nitric acid, perchloride of iron, and sulphate of peroxide of iron decompose alizarin under production of phthalinic and oxalic acid,  $C_{20}H_6O_6 + O_8 = (2HO + C_{16}H_4O_6) + 2C_2O_3$ . If we boil mordanted stuffs with alizarin and water, they assume a beautiful, mostly red color.

*Purpurin* (Rubiacin):  $C_{18}H_6O_6$ . From the solution in alkali carbonates, purpurin is precipitated by an acid in yellow flakes. We obtain purpurin the most readily, if madder be mixed with water, and this mixture be caused to ferment by the influence of yeast at  $20^\circ$  to  $24^\circ$ . When the fermentation is terminated, the mass is boiled out with an alum solution. From the hot filtered solution purpurin separates partially during

\* Madder contains also a colorless body consisting of  $C_{14}H_8O_9$ , which, by boiling with dilute acids, decomposes into formic acid and a green acid  $C_{12}H_6O_5$  (*vide* above, Viridinic Acid).

the cooling, and is purified by recrystallization from alcohol and ether. It crystallizes from an absolute alcoholic solution in red needles, and from an aqueous alcoholic solution in fine, orange-colored needles; crystals from the latter lose 1 atom water at  $100^{\circ}$ , and, therefore, consist of  $C_{18}H_6O_6 + aq.$  The solutions in water and in alcohol possess a red color. The alkaline solution is cherry-red, without appearance of blue. Purpurin is rather easily dissolved in a hot alum solution. If dissolved in ammonia it gives a purple-red precipitate, with salts of baryta, of lime, and of lead. It is sublimable, under partial decomposition. Oxidizing bodies, particularly nitric acid, decompose purpurin under production of phtalinic and oxalic acid.

*Garancin*. *Garancin* is a pigment formed by treatment of madder with concentrated and also with dilute sulphuric acid; the free acid is washed away with water. It possesses a stronger power of coloring than madder. Without doubt, the acid decomposes the, as yet present, rubian, whereby the quantity of alizarin is increased. If animals are fed with madder, their bones assume a red color.

*Anchusin*. *Anchusin* (Alkanna-red):  $C_{35}H_{20}O_8$ , a resinous coloring matter, which occurs in the root of *Anchusa tinctoria*. The roots extracted with water and again dried, are digested with alcohol, and, under addition of hydrochloric acid, the alcohol is distilled off. From the residue the coloring matter is extracted by ether. A dark-red mass; insoluble in water; soluble in alcohol, ether, turpentine oil, and fatty oils with carmine color; is dissolved in alkalis with blue color; acids reproduce the red color. The alcoholic solution gives, with chloride of tin, a carmine-red precipitate, with vinegar of lead a blue, and with salts of peroxide of iron a dark-violet precipitate; alum produces no precipitate. If the alcoholic solution be evaporated without addition of hydrochloric acid, there remains a dark-gray residue, from which ether extracts a green body—*anchusa-green* (alkanna-green),  $C_{34}H_{22}O_4$ .

*Brazilin*. *Brazilin*:  $C_{36}H_{14}O_{12}$  (?), is found in Pernambuco wood (*Cæsalpinia echinatia*) and in Brazil wood (*Cæsalpinia sapan, crista, and vesicaria*). Crystallizes in small orange-colored needles; soluble in water, alcohol, and ether, with red color; acids color the solutions yellow. Gives, with alkalis, purple compounds, and red and violet ones with the oxides of metals.

*Carthamin*. *Carthamin*:  $C_{14}H_8O_7$ . The flowers of *Carthamus tinctorius* (bastard saffron) contain a red (carthamin) and a yellow coloring matter. The latter is soluble in water, the former in carbonate of soda. From the solution in carbonate of soda nearly saturated with acetic acid, clean cotton-wool takes up the red coloring matter, which can be again withdrawn by a soda



solution. Appears, after precipitation with citric acid, as a slimy, deep-crimson mass, which, dried in thin layers, possesses a green, metallic lustre, like cantharides. Scarcely soluble in water, but easily soluble in alcohol, with splendid red color. If we boil the alcoholic solution, we obtain a yellow body,  $C_{14}H_7O_9$ . The alkaline solution soon changes in the air. The *yellow coloring matter* consists of  $C_{24}H_{15}O_{15}$ ; from its aqueous solution, when exposed to the air, a brown body is precipitated, which consists of  $C_{24}H_{12}O_{13}$ .

*Carmine* (Carminic Acid):  $C_{23}H_{14}O_{16}$ , is found in <sup>Carmine.</sup> cochineal (*Coccus cacti*), the wingless female of an insect nestling upon different species of cactus; this insect belongs to the family of the gall-fly, and is killed with hot water. The cochineal is boiled with water, precipitated with vinegar of lead, and the obtained precipitate decomposed by hydrosulphuric acid. Appears as a purplish-brown, pulverizable mass, which dissolves in water and alcohol in every proportion, and is insoluble in ether. By sulphuric and hydrochloric acid, carmine is dissolved without decomposition. The aqueous solution is not precipitated by alkalis. The alkaline earths produce a purple-colored precipitate, alum, upon addition of ammonia a carmine-red, and tin salts a scarlet-red precipitate. If we treat carmine with nitric acid, we thus obtain nitric and nitrococcusic acid,  $C_{16}H_5O_6, 3NO_4 + 2HO$ , which crystallizes in yellow rhombic plates; soluble in water and ether, and especially in boiling alcohol. Carmine belongs to the most durable and beautiful coloring matters. A solution in ammonia gives the most delicate red ink. With the coloring matter of cochineal that of *Coccus ilicis* ("Kermes") quite agrees. Also the coloring matter of *Coccus ficus* and *Coccus polonicus* do not appear to differ from the above. *Coccus polonicus* contains much fat, which can be removed by expression. *Is said to be identical with rufimorinic acid.*

*Hæmatoxylin* (Hæmatin):  $C_{40}H_{17}O_{15}$ . The aqueous extract of Campeachy wood (logwood) is extracted by shaking with ether, or by a displacement apparatus, the ether is distilled off from the extract, and the residue, mixed with water, is left to spontaneous evaporation. Crystallizes in transparent right-angled columns, which contain 8 atoms of water; the color varies between straw-yellow and honey-yellow, without admixture of red; gives a pale yellow powder, and possesses a permanent sweet taste. The crystals become reddish in the sunlight. A solution of hæmatoxylin in ammonia, when exposed to the air, by degrees becomes dark-red, under production of hæmatein-ammonia; the slightest trace of ammonia immediately imparts a red color to hæmatoxylin, by access of air. Potassa immediately produces in the solution, exposed to the air, a violet precipitate, and, later, a blackish-brown one. Hydrates of the earths, oxide of zinc, of bismuth, of nickel,

Coloring matters of Campeachy wood.



etc., completely precipitate hæmatoxylin from the solution, and form, by access of air, purple and blue compounds.

*Hæmatein*.  $\text{Hæmatein} : \text{C}_{40}\text{H}_{14}\text{O}_{15}$ . From the solution of hæmatein-ammonia (*v. Hæmatoxylin*) hæmatein is precipitated by acetic acid. Exhibits, in moist state, a reddish-brown swollen mass; dried, it is dark green, of metallic lustre, and, in thin layers, red, by transmitted light. The alcoholic solution is reddish-brown, the etheric amber yellow; soluble also in water, hydrochloric acid, and dilute sulphuric acid. If we bring zinc into the red acid solution, it assumes a reddish-brown color, and upon addition of ammonia, an almost white precipitate is formed. The *ammonia compound* crystallizes in violet, microscopic quadrilateral prisms; it dissolves in water, with purple color; by evaporation, the ammonia is evolved. In the solution of hæmatein-ammonia acetate of lead gives a dark blue precipitate, iron-alum a black, and protochloride of iron a violet one.

*Santalin*. *Santalin* (Santalic Acid):  $\text{HO}, \text{C}_{30}\text{H}_{13}\text{O}_9$ . This resinous coloring matter is obtained by extracting red wood (*Pterocarpus santalinus*) with alcohol, precipitating the extract with acetate of lead, decomposing the precipitate with sulphuric acid in the presence of alcohol, and evaporating the alcoholic solution. Forms beautiful red microscopic crystals, insoluble in water, soluble in alcohol with red color, in ether with yellow; dissolves in cold concentrated sulphuric acid, without decomposition. It completely saturates the bases; is dissolved in the alkalis and alkaline earths with violet color; the compounds, with the earths and metallic oxides, exhibit pulverulent violet bodies. The *baryta compound* consists of  $\text{BaO}, \text{C}_{30}\text{H}_{13}\text{O}_9$ , and the *lead combination* of  $2\text{PbO}, \text{HO} + \text{C}_{30}\text{H}_{13}\text{O}_9$ . In redwood, several other indifferent substances are said to occur, as *Santalid*, *Santaloid*, *Santalidid*, and *Santalödid*, whose existence, however, is doubtful.

*Curcumin*. *Curcumin* is found in the root of *Curcuma longa* (turmeric). Separates from the etheric solution in inodorous, translucent, uncrystalline scales; gives a yellow powder; melts at  $40^\circ$ ; scarcely soluble in water, but easily in alcohol, ether, the fatty and the volatile oils. The alcoholic solution is said to precipitate glue. Is dissolved in concentrated mineral acids with crimson color, and in alkalis with brownish-red.

*Euxanthin*. *Euxanthin* ("Purree," *India-yellow*):  $\text{C}_{40}\text{H}_{16}\text{O}_{21}$ , is found, in combination with magnesia, in *India-yellow*, which comes from India and China, under the name of *purrée*. Is said to come from the urine of the camel, after partaking of *Mangostona mangifer*. According to other accounts, it must be the juice of an unknown plant, pressed with magnesia. The crude purrée is boiled out with water, and the euxanthin-magnesia remaining is decomposed, at boiling heat, by hydro-

chloric acid. The euxanthin, which separates during the cooling, is obtained, from the alcoholic solution, in long, pale-yellow needles of silken lustre; tastes bitter-sweet, little soluble in alcohol, ether, and cold water. Gives, by dry distillation, besides carbonic acid and water, *Euxanthon* (Purrenon), which appears in large crystals, and consists of  $C_{14}H_4O_4$ ; is also obtained, if a solution of euxanthin, in concentrated sulphuric acid, be boiled with much water. By the action of chlorine and bromine upon euxanthin, we obtain products of substitution,  $=C_{40}H_{14}Cl_2$  (or  $Br_2$ )  $O_{21}$ , which crystallize in yellow needles, and in their properties agree with euxanthin. Nitric acid decomposes euxanthin under production of three nitrogen acids, namely, *Nitropurreeic Acid*:  $C_{40}H_{15}O_{21}NO_4$ , *Cokkinonic* and *Oxyphikrin-nitric Acid* (p. 204). With concentrated sulphuric acid, we obtain the paired hæmathionic acid. Euxanthin easily dissolves in alkalis, with yellow color; from concentrated solutions of carbonates of the alkalis, euxanthin expels the carbonic acid at boiling heat, and, after cooling, we obtain crystalline compounds, which are easily soluble in pure water. The ammonia compounds give, with chloride of calcium and chloride of barium, yellowish-white gelatinous precipitates; the combinations, with the oxides of heavy metals, are yellow and gelatinous.

*Luteolin*. In dyers' weed (*Reseda luteola*), a plant extensively diffused in Europe, is found, particularly in the tips of the flower, a beautiful and durable yellow coloring matter, which appears in golden yellow spangles, soluble in water, alcohol, and ether. It is dissolved in nitric acid, with orange color, and, in concentrated sulphuric acid, with yellowish red. Gives, with alkalis, golden yellow compounds, which are slowly decomposed in the air. Alum, sugar of lead, and acetate of copper, give yellow precipitates in the luteolin solution. In *Serratula tinctoria* (saw-wort) and *Genista tinctoria*, are similar coloring matters to those contained in *Reseda luteola*.

*Orellin*:  $C_{16}H_{13}O_2$  (?). Under the capsules of *Bixa orellana*, a South American tree, is found a resinous, glutinous, bright-red coloring matter, which is called orlean, and consists of a red, resinous (orellin), and a yellow extractive coloring matter. It exhibits a dark reddish-brown powder, which dissolves in concentrated sulphuric acid, with indigo-blue color. The alcoholic solution of orlean gives, with alum, a dark vermilion precipitate, with tin salts, a roseate, with sugar of lead, a brick-red, and, with iron salts, a brown precipitate.

*Gentianin*:  $C_{14}H_5O_5$ , is found in the root of *Gentiana lutea*. The root is extracted with ether, the ether distilled off, and the residue digested with alcohol. After evaporation, we obtain impure gentianin, which is washed with a little cold alcohol and ether, until all the bitter principle is with-

drawn. Crystallizes in fine light yellow needles; tasteless, dissolves in 3630 parts cold water, more easily in ether, and most easily in boiling alcohol. In alkalies, it is soluble with golden yellow color; sublimes, partially, at from  $300^{\circ}$  to  $400^{\circ}$ . From the solution in concentrated sulphuric acid, it is precipitated by water, unchanged. From a solution in concentrated nitric acid (sp. gr. 1.42), water precipitates nitrogentianin,  $C_{14}H_4NO_4O_5 + HO$ . With chlorine, we obtain products of substitution. With alkalies, gentianin gives crystallizable compounds, which contain 2, 3, 4, and 6 atoms gentianin to 1 atom of base. The alcoholic solution of gentianin gives, with baryta water, an orange-colored precipitate,  $= BaO, C_{14}H_5O_5$ ; with acetate of lead, upon the addition of a little ammonia, we obtain a yellow precipitate,  $= 2PbO, C_{14}H_5O_5$ .

Plumbagin.

*Plumbagin* is found in the root of *Plumbago Europæa*. Crystallizes, from alcohol, in yellow pulverizable prisms; slightly soluble in water, but easily in alcohol and ether. The solutions in alkalies have a beautiful cherry color. Gives a red precipitate with vinegar of lead.

Coloring matter of buck-thorn berries. (*Rhamnus tinctoria*.)

The buck-thorn berry (Persian berry, *Granis d'Avignon*), occurring in commerce, has different appearances. The large are a light olive green, and contain chrysorhamnin, the small variety is brown, and has xanthorhamnin as coloring matter. *Chrysorhamnin*:

*Chrysorhamnin*.  $C_{23}H_{11}O_{11}$  (?), is extracted from the unripe berries, by ether. Possesses a beautiful golden yellow color, and can be obtained in ciliary needles, of silken lustre. Insoluble in water, soluble in alcohol and ether. The alcoholic solution gives, with sugar of lead, a beautiful yellow precipitate. *Xanthorhamnin*:

*Xanthorhamnin*.  $C_{23}H_{12}O_{14}$ , is formed, if chrysorhamnin be boiled with water exposed to the air, and can be extracted from the dark-colored berry, by boiling with water. Appears as a dark extract-like mass, soluble in water and alcohol, but insoluble in ether. From the green berries of *Rhamnus cathartica* a coloring matter can be obtained, by boiling with water. This matter crystallizes from the alcoholic solution in grains, and dissolves in alkalies, with saffron yellow color. The *Juice-green* is obtained from the unripe berries, by fermentation.

After fermentation, the juice is expressed and evaporated with alum and potash; it is colored red by acids, and yellow by alkalies.

*Fourth Group.*

## INDIFFERENT COLORLESS VEGETABLE MATTERS.

Whilst the tannins, the lichen acids, and, in part, the coloring matters, exhibit well-characterized groups of organic combinations, there are, in the substances which are described in this group, no accordant chemical relations observed, at least not to a like extent. Many possess a more or less bitter taste, and are, therefore, generally called bitter principles, whilst others are distinguished by a sweet taste. Several possess, like tannin, lichen acids, and coloring matters, weak acid properties; others unite with acids as well as bases; whilst a third class is distinguished as completely indifferent. Always according to their elementary constitution are they soluble or insoluble in water; those therein insoluble dissolve in alcohol, and several, also, in ether; they are nearly all non-volatile. In pure state they possess the capability of crystallizing. Many of these bodies are, as yet, known only as dark-colored extractive masses; several of the same are absorbed by animal charcoal from their aqueous solution, which treatment can aid in obtaining them in a pure state. If, for instance, we boil the aqueous extracts of plants with bone-black (from which all the salts are withdrawn by hydrochloric acid) until they lose their bitter taste, thus can they be obtained crystalline, by withdrawing them from the coal by alcohol, and then evaporating.

Most substances of this group are combinations of a higher order, and, like tannin and lichen acids, may be divided into different matters, partly by the process of fermentation, and partly under the action of dilute acids and alkalies. Thus phloridzin separates into sugar and phloretin, salicin into sugar and saligenin; amygdalin into sugar, oil of bitter almonds, and hydrocyanic acid. Under like treatment athamantin divides into oresolon and valerianic acid, peucedanin into oresolon and angelic acid; and it may be mentioned that other substances, by more particular investigation, would give similar results. The number of these compounds is very large; however, only the most important of them can find a place in this work.

## BITTER PRINCIPLES.

*Phloridzin*:  $C_{24}H_{16}O_{14} + 12aq$ , is found in the root-  
bark of many fruit-trees, particularly *Pyrus malus*,  
and other species of this family. We extract the bark with weak alcohol at  $50^{\circ}$ , and distil off the alcohol. Crystallizes from the aqueous solution in pale-yellow, silken needles; easily soluble in

Some general  
relations of  
these com-  
pounds.

Phloridzin.



alcohol and ether, soluble in 1000 parts cold water, and in all proportions in boiling. Inodorous; tastes at first bitter, then astringent; melts at  $104^{\circ}$  in its water of crystallization; is again solid at  $130^{\circ}$ , and at  $160^{\circ}$  completely fluid. Not volatile; when heated with peroxide of manganese and dilute sulphuric acid, it gives formic acid; chlorine and bromine convert it into resinous masses, insoluble in water. Decomposes under the action of dilute acids into phloretin,  $C_{12}H_6O_4$ , and sugar,  $C_{24}H_{16}O_{14} + 2H_2O = C_{12}H_6O_4 + C_{12}H_{12}O_{12}$ , and if it be simultaneously exposed to the action of oxygen and ammonia, it thus is converted into colored phloridzein. Towards bases phloridzin behaves as a weak acid, and gives, with the alkalis, easily soluble compounds of definite proportions.

**Phloretin.** *Phloretin:*  $C_{12}H_6O_4$ . If we warm the solution of phloridzin in weak sulphuric acid to  $90^{\circ}$ , during the cooling, phloretin separates in white, crystalline, sweet-tasting leaflets. Little soluble in water, almost insoluble in ether, easily soluble in alcohol, wood-spirit, and warm acetic acid. Gives, with nitric acid, a nitrogen compound,  $C_{26}H_{11}(NO_4)O_8(?)$ . It combines with bases; the lead compound consists of  $2PbO, C_{12}H_6O_4$ .

**Phloridzein.** *Phloridzein:*  $NC_{21}H_9O_8(?)$ . We obtain phloridzein from phloridzin in a similar way as orcein (page 408) from orcin. It has the appearance of a red resin; solid; not crystallizable; of shining fracture; dissolves in water with red color; scarcely soluble in alcohol and ether. *Phloridzein-ammonia* possesses a brownish-purple color; is not crystallizable; tastes ammoniacal, bitter; dissolves in water with a splendid blue color. The solution is instantly bleached under the action of deoxidizing agents, and in the air again assumes the blue color; shows generally the reactions of orcein, and in part like indigo.

**Salicin.** *Salicin:*  $C_{26}H_{18}O_{14}$ , is found in the bitter-tasting willow bark, as in *Salix fissa, helix, purpurea, rubra*, etc., in poplar bark, and in *castoreum*. We boil out willow bark with water, digest the evaporated extract with oxyhydrate of lead, remove the dissolved oxide of lead with hydrosulphuric acid, evaporate, and obtain from the syrup-thick fluid the crystals of salicin, which are purified by recrystallization. Very bitter, white crystals; soluble in every proportion in boiling water and in 17 parts at  $19^{\circ}$ ; easily soluble in alcohol, insoluble in ether; melts at  $100^{\circ}$ , and stiffens to a crystalline mass; indifferent; decomposes, under the action of emulsion and dilute acids, into sugar and saligenin,  $C_{26}H_{18}O_{14} + 2H_2O = C_{14}H_8O_4 + C_{12}H_{12}O_{12}$ ; gives chloranil by treatment with chlorate of potassa and hydrochloric acid, and, by distillation with acid chromate of potash and sulphuric acid, gives formic, carbonic, and salicylic acid. If we let chlorine act upon salicin, we obtain compounds of sugar with the known substitution products of saligenin, which are divided under the action of emulsin into sugar and chlorsaligenin. If we shake 1

part salicin with 10 parts dilute nitric acid, when the salicin is dissolved, there separate small white needles of *Helicin*,  $C_{52}H_{35}O_{31}$ , easily soluble in alcohol and boiling water. Under the influence of emulsin, *helicin* decomposes into sugar and salicylous acid,  $C_{52}H_{35}O_{31} + HO = 2(C_{12}H_{12}O_{12}) + 2(C_{14}H_6O_4)$ . By the action of chlorine and bromine upon *helicin*, we obtain compounds of sugar with the substitution products of salicylous acid; these products are divided by emulsin in the same manner as salicin.

*Helicoïdin*:  $C_{52}H_{34}O_{28} + 3HO$ . If salicin be dissolved in *very* dilute nitric acid, we obtain *helicoïdin*, which quite resembles salicin, and, under the influence of emulsin, decomposes into sugar, saligenin and salicylous acid,  $C_{52}H_{34}O_{28} + 3HO = 2(C_{12}H_{12}O_{12}) + C_{14}H_8O_4 + C_{14}H_6O_3$ .

*Saliretin*:  $C_{14}H_6O_2$ , separates from the solution of salicin in dilute mineral acids as an amber-yellow resinous mass.

*Rutilin*:  $C_{28}H_{12}O_4$ , is formed if salicin be brought into concentrated sulphuric acid at  $40^\circ$ . Is known only in combination with sulphuric acid  $= C_{28}H_{12}O_4 \cdot SO$ . *Rutilin-sulphuric acid* appears, after drying, as a beautiful violet powder; insoluble in water, alcohol, and ether; it combines with bases.

*Rufin*:  $C_{28}H_{14}O_{10}$ , is obtained if salicin be brought in small quantities into concentrated sulphuric acid at ordinary temperature, as well as by heating phloridzin. A red, resinous, brittle mass; gives, with sulphuric acid, a paired acid  $= HO(C_{28}H_{14}O_{10} \cdot SO_3) \cdot SO_3$ .

*Olinin*:  $C_{28}H_{12}O_8$ , is formed if a large quantity of salicin be brought into concentrated sulphuric acid at  $78^\circ$ ; olive-green powder; insoluble in water, alcohol, and ether.

*Caïncin* (Caïnce-säure):  $C_{48}H_{39}O_{21}$ , is found in the root-bark of *Chiococca racemosa* in addition to coffee tannin. The bark of the root is boiled out with alcohol, then, by a solution of acetate of lead, the tannin is first precipitated, and from the abfiltered solution the caïncin precipitated by vinegar of lead, and the obtained pale-yellow precipitate decomposed by hydrosulphuric acid. Crystallizes in white, silken, inodorous needles; soluble in water and alcohol. Alkalies produce no change in the solution. Dilute, sulphuric, hydrochloric, and nitric acid divide caïncin into chiococcin (chiococcic acid),  $C_{36}H_{27}O_9$ , and sugar:  $C_{48}H_{39}O_{21} = C_{36}H_{27}O_9 + C_{12}H_{12}O_{12}$ . A solution of acetate of lead with a solution of caïncin gives a white precipitate, which consists of  $3PbO, C_{48}H_{39}O_{21}$ ; with vinegar of lead, we obtain a compound  $= 5PbO, C_{48}H_{39}O_{21}$ .

*Chiococcin*, by mixing the alcoholic solution with water, is separated in the form of a jelly, which dries

to a transparent horn-like mass; easily pulverized; insoluble in water, soluble in alcohol.

*Olivil.*  $C_{28}H_{18}O_{10}$ . If the gum which flows from the wild olive-tree be treated with boiling alcohol, there separates by cooling olivil, in stelliform-grouped needles; inodorous; of bitter-sweetish taste; melts at  $120^{\circ}$ , and stiffens to an amorphous, resinous, idio-electrical mass. It dissolves in water and in ether, and in every proportion in boiling alcohol. By dry distillation it gives pyro-olivinic acid,  $C_{20}H_{13}O_5(?)$ ; decomposes under the influence of oxidizing bodies; nitric acid colors it red-dish-yellow, and concentrated sulphuric acid blood-red; weak acids produce no change.

*Amygdalin.* *Amygdalin*:  $NC_{40}H_{27}O_{22}$ , is found in the family of *drupaceæ*, particularly in bitter almonds, in the stones of the apricot, peach, and cherry in common with emulsin. The bitter almonds, freed from fatty oils by expression, are boiled with alcohol a short time, and the fluid strained through a cloth. The oil, which separates after a few days, is taken away; afterwards the alcoholic solution is heated, filtered whilst hot, and the alcohol mostly distilled off. The residue is mixed with ether, whereby the amygdalin is separated crystalline. Crystallizes from the alcoholic solution in white, shining scales; inodorous, of agreeable, bitter taste; insoluble in ether, easily soluble in water and boiling alcohol; not poisonous, and appears in part to pass into the urine unchanged. Under the influence of emulsin it decomposes into hydrocyanic acid, sugar, and oil of bitter almonds,  $NC_{40}H_{27}O_{22} = NC_2H + 2C_{12}H_{10}O_{10} + C_{14}H_6O_2$ .

Towards reagents amygdalin behaves quite like a paired compound of hydrocyanic acid, sugar, and oil of bitter-almonds. If we boil amygdalin with baryta water, ammonia is evolved under production of amygdalinic acid, a gummy, acid-tasting mass, soluble in water, and insoluble in alcohol.

*Amygdalinic acid.* *Amygdalinic Acid* consists of  $HO, C_{40}H_{26}O_{24} = 2C_{12}H_{10}O_{10} + C_{14}H_6O_2 + C_2HO_3$ ; it may, therefore, be considered as a paired compound of formic acid, sugar, and oil of bitter almonds.

*Myronic acid.* *Myronic Acid*. As bitter almond-oil is furnished by amygdalin under the influence of emulsin, so is mustard-oil formed from myronic acid by myrosin. It is found in black mustard in union with potassa. The mustard-seed, freed from fat by expression, is first completely extracted with alcohol, and then digested with water, which dissolves the myronate of potassa. The aqueous solution is evaporated to the thickness of extract, and the residue treated with weak alcohol, in which the myronate of potassa is found. By evaporation we obtain myronate of potassa, which is purified by washing with weak alcohol. From the potassa salt we separate the myronic acid, by tartaric acid and

alcohol; it remains, after evaporation, as an inodorous, bitter, and sour mass, not crystalline. The alkali salts crystallize. Myronic acid contains nitrogen, carbon, hydrogen, oxygen, and sulphur. (*Compare Mustard Oil*, p. 327).

White mustard contains no myronic acid, and hence gives no mustard oil; in it, on the contrary, a crystallizable substance, *sinapin*—occurs, which contains sulphur; by myrosin it is decomposed into a bitter, sharp principle, and, probably, into hydrosulphocyanic acid.

*Athamantin*:  $C_{24}H_{15}O_7$ , is found in the root of *Athamantin*. *Athamanta oreoselinum*. From the etheric solution of the alcoholic extract, athamantin is separated oily, and stiffens by degrees to a crystalline mass. It is obtained pure by being dissolved in alcohol, precipitated by water, and repeatedly crystallized. Forms colorless quadrilateral prisms, often an inch in length; possesses a rancid, soap-like odor, and a sharp, irritating taste. Insoluble in water; melts in boiling water to an oil, which stiffens crystalline; easily soluble in alcohol and ether; melts at  $79^\circ$ ; non-volatile; under the influence of alkalies, it decomposes into *oresolon*,  $C_{14}H_5O_3$ , and valerianic acid,  $C_{24}H_{15}O_7 = C_{14}H_5O_3 + C_{10}H_{10}O_4$ . With dry hydrochloric acid gas it gives a crystalline mass.

*Peucedanin*:  $C_{24}H_{12}O_6$ , is found in the root of *Peucedanin*. *Peucedanum offic.*, and is obtained by extraction of that substance by alcohol. Crystallizes from the etheric solution in small hexagonal prisms, melts at  $75^\circ$ , insoluble in water, not easily soluble in cold alcohol, easily soluble in boiling alcohol, ether, and volatile oils. Gives, with dilute nitric acid, a nitrogen compound,  $C_{24}H_{11}NO_4O_6$ , which, with ammonia, forms an amid combination. From the solutions of peucedanin, in alkalies, it is precipitated by acids. It may be regarded a combination of oresolon with angelic acid,  $C_{14}H_5O_3 + C_{10}H_7O_3 = C_{24}H_{12}O_6$ . In the root is also found a small quantity of a body soluble in ether—the *Oxypeucedanin*:  $C_{24}H_{11}O_7$ .

*Oresolon*:  $C_{14}H_5O_3$ . Separates from the hot alcoholic solution in small, colorless, inodorous, and tasteless needles, insoluble in water, and soluble with difficulty in ether and in alcohol; non-volatile. If hydrochlorate of athamantin be boiled with water, we thus obtain crystals which consists of  $C_{14}H_5O_3$ . *Oresolon*.

*Absynthiin*:  $HO, C_{16}H_{10}O_4$ , is found in wormwood *Absynthiin*. (*Artemisia absinthium*). We shake the alcoholic extract with ether, evaporate the etheric solution, and treat the residue with a little ammonia, in which a brown resin is dissolved. Possesses a brownish-yellow color; a disagreeable odor, like wormwood; tastes extremely bitter; is soluble with difficulty in water, easily soluble in alcohol, and not so easily in ether, reacts acid, is



dissolved in alkalis with golden-yellow color. The solution in concentrated sulphuric acid is colored, in the air, a deep indigo-blue.

*Aloin*:  $\text{HO}, \text{C}_{34}\text{H}_{18}\text{O}_{14}$ , is found in aloes, the dried juice of *Aloë socotorina*, *purpurescens*, *spicata*, etc.

These are infused with water, and the infusion evaporated in a vacuum. After some time, we obtain crystals of aloin, which are purified, by recrystallization, from alcohol. Stelliform-grouped prismatic crystals; tastes first sweet, and afterwards intensely bitter, slightly soluble in cold water, but easily in warm water and warm alcohol. It is easily absorbed by pure alkalis and their carbonates with golden color. If we boil it a short time with alkalis or with strong acids, it is converted into a dark-brown resin. With concentrated nitric acid it furnishes chrysaminic acid, and, by dry distillation, gives an aromatic-smelling volatile oil. With bromine, we obtain a product  $= \text{C}_{34}\text{H}_{15}\text{Br}_3\text{O}_{14}$ .

*Appiin*:  $\text{C}_{24}\text{H}_{14}\text{O}_{13}$ , is found in parsley (*Apium petroselinum*). The completely dry and pulverized aqueous extract is boiled out with alcohol, the alcohol distilled off, and the deposited appiin purified by expression with a little alcohol. Light, flocculent, nearly colorless, tasteless, and inodorous powder, amorphous, and indifferent; is dissolved in 8500 parts cold water, but dissolves easily in boiling water; by cooling, the solution gelatinizes; the hot alcoholic solution also forms, after cooling, a stiff jelly. If the aqueous solution be a long time boiled, it loses the capability of gelatinizing, and forms a body which consists of  $\text{C}_{24}\text{H}_{16}\text{O}_{15}$ . If, on the contrary, it be boiled with dilute acids, water escapes, and we obtain a compound which consists of  $\text{C}_{24}\text{H}_{10}\text{O}_9$ ,  $\text{C}_{14}\text{H}_{12}\text{O}_{11}$ , etc. The solution of appiin gives a dark red fluid, with sulphate of peroxide of iron. This body differs from pectinic acid in its solubility in alcohol.

*Aesculin* (Polychrom):  $\text{C}_{16}\text{H}_9\text{O}_{10}$ . If the bark of horse-chestnut, of the ash, or of quassia, be extracted by hot water, we obtain a fluid which appears yellow by transmitted light, and blue by reflected. The substance thus dissolved out is aesculin, which separates, if the alcohol be distilled from the alcoholic extract of the bark, and the residue left a long time in the cold. Crystallizes from the hot alcoholic solution, by very slow cooling, in microscopic needles; appears, generally, as a white, inodorous, loose powder; tastes slightly bitter, dissolves in 12.6 parts boiling water, and in 672 parts at  $10^\circ$ , not easily soluble in alcohol, insoluble in ether. Only a trace of aesculin gives an iridescent solution; acids diminish this property, alkalis increase it. Hydrochloric acid colors the aesculin solution red, and at last, dark yellow; thereby the iridescence disappears.

*Anthiarin*:  $\text{C}_{14}\text{H}_{10}\text{O}_5$ , is found in *Upas antiar*, an extract procured from *Antiaris toxicaria*, with which

the inhabitants of the Indian Archipelago poison their arrows. If the extract be boiled out with alcohol, the anthiarin crystallizes, by cooling, in silvery, inodorous leaflets, of mother-of-pearl lustre; soluble in 251 parts water, in 70 parts alcohol, and in 2792 parts ether; melts at  $220^{\circ}$ ; non-volatile. A millegramme, brought into a wound, produces vomiting, convulsions, and death.

**Cocculin** (Picrotoxin):  $C_{10}H_6O_4$ , is found in the Cocculin. kernels of *Menispermum cocculus*. The kernels, freed from fat, are digested with alcohol, and the last distilled off; the cocculin, which separates, is recrystallized from aqueous alcohol. Transparent leaflets, inodorous, tastes extremely bitter, dissolves in 25 parts boiling water, and in 150 parts cold; boiling alcohol dissolves 0.33 and ether 0.4. Taken internally, it produces dizziness, convulsions, and death; easily soluble in alkalies.

**Columbin**:  $C_{42}H_{22}O_{14}$ , is found in Columbo-root Columbin. (*Menispermum palmatum*) and can be extracted from that root by ether. Crystallizes in transparent rhombic columns; inodorous; tastes slightly bitter; insoluble in cold water, not easily soluble in alcohol ( $\frac{1}{30}$ th part); melts like wax; easily soluble in alkalies, and, again, precipitable by acids. In *columbo* is found another acid,  $C_{42}H_{23}O_{13}$ , almost insoluble in water and of a bitter taste.

**Chinovin** (Chinovic Acid):  $HIO, C_{38}H_{29}O_9$ , is found Chinovin. in *China nova* and *China piton*. The bark is boiled with lime-milk, and from the filtrate chinovin is precipitated by hydrochloric acid; it is purified by solution in alcohol and precipitation by water. When dried, it is a gummy mass, which, pulverized, gives a dazzling white powder; tastes intensely bitter; insoluble in water, but easily soluble in warm alcohol and ether. Possesses weak acid properties, and combines with bases. The alkali salts are easily soluble in water.

**Limonin**:  $C_{42}H_{25}O_{13}$ , is found in the seeds of the Limonin. lemon and the orange, and is obtained by extraction with alcohol. Microscopic crystals of purely bitter taste; not easily soluble in water, ether, and ammonia; more easily soluble in alcohol and acetic acid, and, particularly, in pure potassa. Dissolves in sulphuric acid with blood-red color; is not changed by concentrated nitric acid.

**Meconin**:  $C_{20}H_{10}O_8$ , is found in opium. Crystal- Meconin. lizes in colorless, inodorous, almost tasteless prisms; melts at  $90^{\circ}$ ; distillable; is dissolved in 18 parts boiling water and 265 parts cold; dissolves in alcohol and ether. Gives, with nitric acid, a nitro-compound; and, with chlorine, the mechloinic acid,  $C_{14}H_7O_{10}$  (?).

**Quassiin**:  $C_{20}H_{12}O_6$ , is found in the wood of *Quassia* Quassiin. *amara* and *excelsa*. If the aqueous extract be digested with alcohol, we obtain this principle pure by repeated crystalliza-

tion from the ethero-alcoholic solution. Small, opaque, inodorous crystals; unchangeable in the air; extraordinarily bitter tasting; are dissolved in 200 parts cold water, more easily soluble in anhydrous alcohol; melt like a resin, and cool to a semi-transparent, brittle mass.

**Santonin.** *Santonin* (Santonin Acid):  $C_{30}H_{18}O_6$ , is found in the flower heads of *Artemisia santonica* and *Judaica* (the so-called worm-seed\*). The seeds are boiled with lime-milk, and the filtered solution is slightly over-saturated by hydrochloric acid. After some time the santonin is deposited, and is purified by treatment with animal charcoal, recrystallization, etc. Crystallizes in flat, compressed, hexagonal columns; colorless, inodorous; tastes, after chewing, a little bitter; becomes yellow in the sunlight; melts at  $168^{\circ}$ ; stiffens crystalline; sublimable, under formation of irritating vapor. Almost insoluble in cold water; dissolves in 250 parts boiling, rather easily soluble in alcohol and particularly in ether, fats, and volatile oils. Forms, with bases, not very permanent salts, mostly soluble in water.

**Saponin.** *Saponin* (Struthiin):  $C_{26}H_{24}O_{16}$  (?), is found in the root of *Gypsophila struthium* and *Quillaja saponaria* (Sapon. offic.). Is separated from the hot alcoholic extract during the cooling. White, not crystalline; of sharp, piquant taste; dissolves in all proportions in water, and gives a foaming solution; not easily soluble in alcohol; insoluble in ether. In contact with alkalis, it is converted into a weak acid, the saponic,  $C_{26}H_{23}O_{12}$  (?).

**Senegin.** *Senegin* (Polygalic Acid):  $C_{22}H_{18}O_{11}$ , is found in the root of *Polygala senega*. White, pulveriform, inodorous; tastes, after a little, very itching; the powder excites violent sneezing; easily soluble in boiling water and alcohol, insoluble in ether; gives no definite compounds with bases.

**Smilacin.** *Smilacin* (Sarsaparillin, Parilline) is found in the root of *Smilax sarsaparilla*, and is extracted from this by boiling with alcohol. Crystallizes in small, colorless, radiated needles. Insoluble in cold water, not easily soluble in hot, or in alcohol, easily soluble in boiling alcohol and in ether. Tastes in solution bitter and aromatic.

In relation to the bitter principles at present known, I refer to my "Chemie der organischen Verbindungen," I. p. 800.

#### SWEET PRINCIPLES.

**Mannit.** *Mannit* (Manna Sugar):  $C_{12}H_{14}O_{12}$ , is the principal constituent of manna, which is obtained by drying the juice flowing spontaneously from the *Fraxinus ornus*, ro-

\* Seeds of *Chenopodium anthelminticum* (which had superseded the seeds of *Artemisia*), are universally known in the U. S. as worm-seed. D. B.



*tundifolius*, and *excelsior*. It is farther found in the juice exuded from several cherry and apple trees, in the alburnum of several species of *Pinus*, in the root of the pomegranate-tree, in different mushrooms in the bark of *Canella alba*, in the honey-dew of the linden, and is formed under certain conditions by fermentation of sugar with lactic acid. If manna be boiled out with alcohol, during the cooling, mannit is deposited in colorless needles. Of disagreeable sweet taste; melts at  $166^{\circ}$ ; stiffens crystalline; easily soluble in water, and forms a syrup; scarcely soluble in cold alcohol, rather soluble in boiling. Without action upon polarized light. Gives, with concentrated nitric acid, *nitromannit*, Nitromannit, a violently exploding compound  $= C_{12}H_8(6NO_4)O_{12}$ , which is obtained when finely-ground mannit, with some nitric acid of 1.5 sp. gr., is stirred, until perfect solution takes place, and then alternately so much nitric and sulphuric acid added that to 1 part mannit, there comes  $4\frac{1}{2}$  parts  $HO, NO_3$  and 10 parts  $HO, SO_3$ . The nitromannit, which separates, is washed with cold water, and left to crystallize from alcohol. Mannit gives, with sulphuric acid, a paired acid  $= C_{12}H_{14}O_{12} + 8SO_3(?)$ . Mannit also combines with bases, but it forms no definite compounds. A combination isomeric with mannit is *dulcose* (dul-  
cin), whose origin is unknown. Dulcose.

*Glycyrrhizin* (Licorice Sugar):  $C_{16}H_{12}O_6$ , or  $C_{36}$  Glycyrrhizin.  $H_{24}O_{14}$ , is found in licorice wood, the root of *Glycyrrhiza glabra* and *echinata*. The root is boiled out with water, the extract precipitated with vinegar of lead, being cautious that it does not become neutral, the washed precipitate decomposed by hydrosulphuric acid, and the solution, filtered from sulphide of lead, cautiously evaporated. A honey-yellow, not (?) crystallizable mass, soluble in water and alcohol, of peculiar sweet, afterwards itching taste, melts at  $200^{\circ}$ , not volatile, gives, with nitric acid, a nitro-compound, combines easily with acids, bases, and salts. From the aqueous solution it is precipitated by concentrated sulphuric acid. Most metallic salts give precipitates with glycyrrhizin, consisting of the salts and glycyrrhizin.—In the flowers of *Arbus praeatorius*, in the root of *Polypodium vulgare*, *Ononis spinosa*, are found sweet principles which quite agree with glycyrrhizin, and especially are precipitated from their solutions by sulphuric acid.

*Glycerin*:  $C_6H_8O_6 = HO, C_6H_7O_3$ , is formed by Glycerin. transposition, from oxide of glycy, in the saponification of fats. We accurately saturate with sulphuric acid the alkaline mother liquor, from which the soap is separated, evaporate and extract the syrup-thick residue with alcohol. After evaporation of the alcoholic solution, we obtain the pure glycerin as a sweet, colorless, uncrystalline, syrup-thick, inodorous fluid, soluble in all proportions in water and alcohol, and insoluble in



ether. Glycerin dissolves most vegetable acids and all deliquescent inorganic salts; gives, with potassa, also with baryta and oxide of lead, a compound soluble in alcohol. By dry distillation it gives acrolein (p. 143), and, if left a long time in contact with yeast, it decomposes into water and propionic acid. Chlorine and bromine convert it into derived combinations. With sulphuric acid, we obtain a paired acid,  $\text{HO}(\text{C}_6\text{H}_7\text{O}_5, \text{SO}_3) \cdot \text{SO}_3$ , which forms salts soluble in water. Glycerin-phosphoric acid consists of  $2\text{HO}, \text{C}_6\text{H}_7\text{O}_5, \text{PO}_5$ . With nitric acid, glycerin gives a violently exploding, very poisonous nitro-compound.

*b. COMMON VEGETABLE AND ANIMAL MATTERS, OR THE PROXIMATE CONSTITUENTS OF THE VEGETABLE AND THE ANIMAL KINGDOM.*

The common vegetable and animal matters consist: —

1. Of *Carbon, Hydrogen, and Oxygen*;
2. Of *Carbon, Hydrogen, Oxygen, and Nitrogen*.

They divide, therefore, into *Non-nitrogenous* and *Nitrogenous Compounds*.

*1. Non-nitrogenous Combinations.*

According to the proportion of the hydrogen and the oxygen atoms, the non-nitrogenous combinations are divided into: *a. Carbohydrates*, and *b. Pectin-substances*. The former contain hydrogen and oxygen, in the proportion as in water; in the latter, the oxygen exceeds the hydrogen.

*First Group.*

CARBOHYDRATES.

(Hydrates of Carbon.)

The combinations of this group, almost without exception, belong to the vegetable kingdom, and form the non-nitrogenous aliment. The atomic weight of the most of them can only be approximately given, and since their particular constituents are not known, their constitution can only be expressed by empirical formulæ. A few show, in physical relations, certain common properties, and then bear a general appellation; thus we distinguish species of gum, of starch, and of sugar. The relations which the carbohydrates chemically present, their combinations and decompositions, are best explained if we assume for their

atomic constitution, in anhydrous condition, the following empirical formulæ:—

Cellulose,	. . . . .	$C_{12}H_{10}O_{10}$ ,
Starch Species,	$\left\{ \begin{array}{l} \text{Amylum,} \\ \text{Inulin,} \\ \text{Lichenin,} \end{array} \right\}$	$C_{12}H_{10}O_{10}$ ,
Gum Species,	$\left\{ \begin{array}{l} \text{Dextrin,} \\ \text{Arabin (gum),} \\ \text{Vegetable gluten,} \end{array} \right\}$	$C_{12}H_{10}O_{10}$ ,
Sugar Species,	$\left\{ \begin{array}{l} \text{Milk-sugar,} \\ \text{Cane " } \\ \text{Grape " } \\ \text{Fruit " } \end{array} \right\}$	$C_{12}H_{10}O_{10}$ , $C_{12}H_{12}O_{12}$ ,

besides a few other substances not yet particularly investigated.

As appears from this summary, these combinations, with the exception of grape-sugar and fruit-sugar, have the same percentage constitution; they show a great agreement in their chemical relations, and their difference depends principally upon their physical properties; they can, in part, be converted into one another, and this conversion consists essentially in the change of these external characteristics. Carbohydrates appear partly crystalline, as the sugar species, partly as amorphous masses, as the gum species, and partly organized, as cellulose and starch. The sugar species are soluble in water and alcohol; the gum species are precipitated by alcohol from the aqueous mucilaginous solution. Amylum is insoluble in cold water, and in boiling swells like a sponge, without being dissolved; cellulose differs from all other carbohydrates by its insolubility in ordinary solvents. As already stated in the General Part, the compounds of this group are non-volatile, and, by dry distillation, give the products mentioned at page 49.

A few general chemical relations.

Proportions of solubility.

Under the influence of gentle heat, diastase, dilute acids and yeast, the carbohydrates, which consist of  $C_{12}H_{10}O_{10}$ , are converted, at a certain temperature, into fruit-sugar and grape-sugar, which then decompose into alcohol and carbonic acid by exposure to the continued action of yeast. Upon the products, which are formed by the action of other ferments, see the article on "Spontaneous Decomposition," in the General Part. Many compounds of a higher order, as salicin, phloridzin, amygdalin, caïncin, etc., contain carbohydrates, and, under the influence of ferments, decompose into sugar and other products.

Action of acids and ferments.

Behavior of  
carbohydrates  
to polarized  
light.

In respect to the influence, which the carbohydrates exercise upon polarized light, cellulose and starch come not into consideration, on account of their insolubility, in water. With inulin, the rotation is to the left. Of all bodies of the gum species, dextrine possesses the strongest turning power to the right, whilst gum behaves indifferently. With milk-sugar, cane-sugar, and grape-sugar, the power of rotation is to the right; with fruit-sugar, it is to the left. The conversion of these bodies into one another, particularly of gum and starch, into dextrine—cane-sugar and grape-sugar into fruit-sugar, may be most easily known by polarized light.\*

Behavior to  
iodine and to  
the other  
halogens.

Pure cellulose is not colored blue by tincture of iodine; this, however, takes place, if it be boiled a long time with concentrated potash-lye. On the contrary, starch, dry as well as in the form of paste, is immediately colored intensely blue, under production of loose compounds, which, by warming, completely lose the iodine; bromine imparts to the same an orange-red color. The other carbohydrates are only colored brown by tincture of iodine, and to them the halogens generally behave indifferently.

Behavior to  
salts of deut-  
oxide of copper  
in the presence  
of potassa.

If to a boiling solution of inulin we add a few drops of sulphate of deutoxide of copper, and then potassa in excess, we obtain an intense blue solution from which protoxide of copper very soon separates; the solutions of dextrine, of fruit-sugar, and of grape-sugar behave in the same manner, if the blue fluid be warmed. (Detection of sugar in urine.) Cane-sugar also gives a blue solution; but the separation of protoxide of copper does not follow until after long boiling. On the other hand, gum-copper-deutoxyd is not soluble in potassa, and also suffers no change by continued boiling with water.

Behavior to  
oxidizing  
bodies.

All carbohydrates, when heated with *peroxide of manganese* and *dilute sulphuric acid*, give formic and carbonic acid. *Dilute nitric acid* does not act in the cold upon cellulose, but if the latter be exposed to continued boiling with that acid, we obtain oxalic and suberic acid. Starch, dextrine, cane-sugar, grape-sugar, and fruit-sugar, by like treatment, give oxalic and saccharic acid; milk-sugar, gum, and vegetable gluten furnish oxalic and mucic acid. But if the carbohydrates be exposed a short time to the action of concentrated nitric acid, particularly under the co-operation of sulphuric acid, we obtain very violently exploding nitrogen compounds (gun-cotton).

\* Upon the power of rotation of the sugar species, and of the substances related to them, compare my "Chemie der organischen Verbindungen," vol. i. p. 406.

*Dilute sulphuric acid*, as has already been remarked, finally converts the carbohydrates into grape-sugar; cellulose previously changes into starch and dextrine; if we let dilute acid act a long time upon grape-sugar, the solution becomes clouded under production of substances of ulmin and of humin. Other dilute acids have the same influence, particularly phosphoric acid. With *concentrated sulphuric acid* the carbohydrates unite in the cold, forming paired compounds; if they be heated with concentrated acid, they are colored black, under evolution of sulphurous and carbonic acid; by an excess of acid, the organic substance is at last completely destroyed. If we heat a mixture of anhydrous phosphoric acid and cane-sugar, the mass becomes brown; it evolves formic acid and water, whilst humin substances and uncrystallizable sugar remain in the residue. Phosphoric acid appears to form no paired compounds.

Action of sulphuric and phosphoric acids.

If the carbohydrates be heated with hydrate of potassa in excess, we obtain carbonate and oxalate of potassa, under evolution of hydrogen gas. If we let a solution of grape-sugar, saturated with lime or baryta, stand a long time in the air, it thus changes into glucinic acid. Upon the products which are formed by the distillation of a mixture of lime and sugar, compare page 148.

Action of pure alkalies.

Although the carbohydrates belong to the indifferent organic combinations, yet they possess the capability of uniting with bases in definite proportions. The compounds, with alkalies and alkaline earths, are soluble in water, and insoluble in alcohol. If to a solution of gum we add potassa, and then alcohol, gum-potassa is precipitated, which, after washing, is easily dissolved in water; this solution gives, with acetate of lead, a white precipitate of gum-leadoxyd. In like manner, we obtain compounds with the sugar species. The compounds, with the alkalies, react strongly alkaline. These are the only substances by which the atomic weight of the carbo-hydrates can be determined. The insoluble cellulose itself possesses the property of decomposing a few salts with heavy bases, as those of alumina, of peroxide of iron, of tin, etc., in their aqueous solution, into acids and basic salts, and of uniting intimately with the basic salts. (*See Coloring Matters and Mordants.*)

Compounds of the carbohydrates.

Although the non-nitrogenous food is generally eaten in larger quantities than the nitrogenous, yet it can neither in chyle nor in blood be recognized with certainty; only in the liver we constantly find sugar. The physiological importance of these substances is still almost unknown. That they, under certain circumstances, contribute to the production of fat, is already mentioned, p. 189. Some have endeavored to establish the view that they are employed exclu-

Physiological importance.



sively for the process of oxidation and of producing animal heat, an opinion which can scarcely find an advocate. It is more probable that they, by exchange of matter, unite with nitrogenous products of decomposition at the moment of their production, thus forming nitrogenous aliments.

## CELLULOSE.



*Cellulose* (Lignin, Wood Fibrin, Medullin) is the principal constituent of the vegetable kingdom. All vegetable organs are an aggregation of cells, whose membrane, freed from included and foreign matter, exhibits pure cellulose; it is always organized, and is distinguished, as already remarked above, by its insolubility in water, alcohol, ether, dilute alkalies, and acids. Vegetable wool, the pith of plants, bleached paper, etc., may be regarded as

The so-called  
incrusting ma-  
terials.

pure cellulose. Generally, upon the inner side of the cell-membrane, are deposited different substances, upon which depend, especially, the solidity and hardness of wood, and which can often be withdrawn, by long maceration with potassa. The nature of these substances is very different, and we apply to them the name of incrusting matters, by which is to be understood, however, no definite combination. Wood contains, besides these, still other substances, which can be withdrawn by different solvents. Until recently, cellulose was regarded as belonging, exclusively, to the vegetable kingdom, yet we have discovered in the inferior animals, as in the *Ascidie*, a complete tissue of cellulose. The ease with which cellulose is attacked by concentrated sulphuric acid, depends upon its coherence; thus the linen fibre withstands the action rather long, whilst cotton texture is, even in a few minutes, changed into a mucilaginous mass, soluble in the acid.\* (Distinguishing between linen and cotton webs.)—(Employment of vegetable fibre for cloths and paper.—State of moistness of wood, and employment of the latter as fuel.—Cutting wood.) Upon the decay of wood, and the preservation of that substance, by soaking in lye, or by smoking and impregnation with inorganic salts, compare page 55, and my “*Chemie der organischen Verbindungen*,” vol. I. p. 354.

Nitrocellulose.  
Gun-cotton.

*Nitrocellulose* (Xyloidine, Gun-Cotton, Pyroxylin):  $\text{C}_{12}\text{H}_7(\text{NO}_4)_3\text{O}_{10}$ (?). Probably different compounds exist, some of which are soluble in ether, and some insoluble. Completely cleansed and well-dried cotton wool

\* By the action of decaying potatoes, the cellulose is dissolved. By this action the cells, which, in the sound potatoe, inclose the amylum, are first separated, and then their walls dissolved; the same occurrence takes place in the potatoe disease; the putrefaction of the contents is, therefore, only a consequence of the disease.

is dipped 10 to 12 minutes in a mixture of 2 parts  $\text{HO,NO}_3$ , and 3 parts  $\text{HO,SO}_3$ , then thoroughly washed with water and dried in a gentle heat. Instead of nitric acid, nitrate of potassa may be used. Under the microscope, gun-cotton does not appear different from common cotton wool; it explodes very violently, and burns up without leaving a residue, under production of carbonic oxide, carbonic acid, nitrous oxide, and water. It is insoluble in water and in alcohol, but it dissolves in alkalies and in ether. The etheric solution is known under the name of *Collodium*; for its preparation, the cotton exposed to the action of salt-  
petre and sulphuric acid must be employed. If we  
let the solution, thinly spread, evaporate, there remains a transparent, extremely electric, uniform mass (electric paper, production of small balloons, employment of collodium as a means of adhesion in surgery).

*Cork Substance.* Cork substance, in its pure  
state, was viewed, until lately, as identical with cellulose. But it is only very slowly attacked by concentrated sulphuric acid, and dilute nitric acid oxidizes it, even below  $100^\circ$ ; thereby is formed a series of acids, whose extreme members are suberic and succinic acid. It is very difficult to procure cork substance pure; sometimes it forms a thin amorphous adhesive coat over the entire plant; in the potatoe, it forms the external cell layers; it does not transmit water freely; therefore, potatoe with unbroken surface, may be long preserved, and lose only a little in weight. Cork substance differs also in constitution from cellulose.

	Cellulose.	Cork substance of the potatoe.
Carbon . . .	43.99	62.30
Hydrogen . .	6.20	7.15
Oxygen . . .	49.31	27.57
Nitrogen . . . . .		3.03

#### STARCH SPECIES.

1. *Amylum* (Starch, Common Starch-meal):  $\text{C}_{12}\text{H}_{10}\text{O}_{10}$ . 1. *Amylum*.  
 $\text{H}_{10}\text{O}_{10}$ , is widely diffused in the vegetable kingdom; many vegetable substances, as *e. g.* the potatoe, contains, in addition to water, little else than starch. In company with protein compounds, amyllum is found in the seeds of the grain species (*Cerealia*), of the *Leguminosæ* plants (pulse, the cotyledon of the embryo), in the stems of many monocotyledons, particularly the palm species (sago), in the poisonous root of *Janipha manihot* (*tapioca*), in the root of *Maranta arundinacea* (*arrowroot*), and generally in most roots. *Amylum* already exists in the cells of plants, deposited in isolated grains, whose size varies according to the plant in which it occurs, from

$\frac{1}{600}$ th of a line (starch from the seed of *Chenopodium quinoa*), to  $\frac{1}{60}$ th of a line (potatoe starch). These grains have, internally, a central cavity, around which the starch is deposited in equal layers. Starch is a white, soft-feeling, tasteless, and inodorous powder, grating between the teeth, insoluble in water, alcohol, and ether; soluble in dilute acids and alkalies. If a starch be brought into hot water, the layers swell up without being dissolved, and form the so-called paste (Kleister), by which the grains increase in volume thirtyfold. At  $150^{\circ}$  the paste is perfectly fluid, and, gradually, is converted into dextrine and grape-sugar. If iodine be contained in a solution it can be detected by starch, even if the former be almost a million times diluted. If to a solution of borax we add starch paste, the whole is coagulated under production of a combination of starch and borax; dilute acids prevent the production. Solutions of sulphate of deutoxide of copper and sulphate of peroxide of iron, of chloride of barium, and of other salts, give no precipitate with a solution of starch. If tannin be added to a solution of starch, gray flakes are separated, which unite, forming a soft mass.

Starch is obtained when the pap, procured by grinding potatoes, is washed upon a hair sieve so long as the water flows away milky. After some time the starch is deposited from the fluid which has run through. Or we macerate rye or wheat in water until the grain can be crushed between the fingers, grind it to a uniform mass, and knead it in a bag under water until all the starch grains are pressed out. The adhesive substance, with the hulls, remains in the bag.

*Xyloidin.* Fuming nitric acid converts starch into nitro-amylum, which exhibits the so-called *xyloidin*, and probably consists of  $C_{12}H_9(NO_4)O_9$ .

*Uses of starch.* Starch is the most common nutriment in combination with protein substances; as it is insoluble in water it must be first converted into dextrine and sugar. This takes place partly by boiling, and partly by the action of the gastric juice. In baking bread, the starch is mostly converted into dextrine. As means of stiffening, starch paste is much used in calico printing, and in other trades. Employment of starch in the preparation of beer, whiskey, etc.

*Paramylum.* In the infusoria species, *Euglena viridis*, are contained small white grains, which appear similar to wheat-meal, and dried at  $100^{\circ}$  correspond to the formula  $C_{12}H_{10}O_{10}$ ; it is insoluble in cold water and dilute acids; swells up in hot water, without, however, forming a jelly. From the solution in dilute alkalies paramylum is precipitated by hydrochloric acid, in the form of a transparent gelatinous body. By continued boiling with hydrochloric acid, it is converted into

fermentable sugar; at  $200^{\circ}$ , it changes into a tasteless gummy body.

2. *Inulin*:  $C_{12}H_{10}O_{10}$ . Inulin, like starch, is 2. Inulin. widely diffused in nature; it is found in the roots of different *Syngenesiæ*, as in *Inula helenium*, *Helianthus tuberosus*, *Leontodon taraxacum*, and particularly in the bulb of the *dahlia* (*Georgina*). Appears as a white, extremely soft, tasteless, and inodorous powder, adhering to the teeth. Scarcely soluble in cold water, but is perfectly dissolved by boiling water, without forming a paste, and during cooling it is deposited pulveriform. Even by repeated treatment with boiling water, inulin is converted into sugar; if some yeast be added to the aqueous solution, wine fermentation soon sets in. In the heat, it very quickly reduces salts of silver, of copper, and of lead. Is obtained in the same manner as starch.

3. *Lichenin* (Moss Starch):  $C_{12}H_{10}O_{10}$  (?). It appears to be first formed, by boiling with water, from an unknown substance, which occurs in different lichens, as Iceland moss (*Cetraria Islandica*), *Lichen plicatus*, *barbatus*, etc. Sparingly soluble in cold water, insoluble in alcohol; if warm water be poured upon the lichens, they swell to a slimy jelly, not adhesive. It entirely dissolves in boiling water; after the cooling of the thin solution, we obtain a jelly. Quite tasteless; of a peculiar moss odor, and a brown color. We obtain lichenin, if Iceland moss be completely extracted with cold water and some carbonate of potash, and the residue boiled some time with water. We strain it whilst it is hot, and dry the jelly by a gentle heat. Employed in medicine.

#### GUM SPECIES.

1. *Dextrine*:  $C_{12}H_{10}O_{10}$ . That dextrine already 1. Dextrine. exists in the vegetable kingdom, is not, with certainty proved. It is formed by the action of heat and of diastase, which last is evolved in the germination of wheat and of other corn (malt),\* and of dilute acids upon starch. It is best obtained, if 1000 parts starch are uniformly moistened with 2 parts nitric acid and 300 parts water, the mass first dried in the air, and then exposed to the temperature of  $100^{\circ}$ , until it entirely dissolves in water and is no longer colored blue by tincture of iodine. Or, we digest starch paste with 1 to 2 per cent. sulphuric acid, at  $80$  to  $90^{\circ}$ , after the formation of dextrine is terminated, precipitate the sulphuric acid by baryta, evaporate the filtered solution, and from

\* We obtain diastase, if freshly germinated corn (grain) is crushed, stirred with half its weight of water, and expressed. The fluid is first mixed with a little alcohol, then filtered, and the diastase precipitated by a large addition of alcohol. Dried by gentle heat, it appears as a gummy body. Is probably formed from the protein substances.



the concentrated fluid precipitate the dextrine by alcohol; the sugar, simultaneously formed, remains dissolved. Instead of sulphuric acid, grain malt, or diastase, can be employed. A completely amorphous, tasteless, and inodorous mass, resembling gum Arabic; very easily soluble in water, forming a slimy fluid; soluble in aqueous alcohol and insoluble in absolute. Under the action of diastase and dilute acids, it is converted into grape-sugar. (Employment, instead of gum, as stiffening. Use in medicine, dextrine bandages. Constituent of beer, etc.)

2. Arabin. 2. *Arabin* (Gum in a limited sense):  $C_{12}H_{10}O_{10}$ .

It is probably formed in the cells of plants, whose walls imbibe the aqueous solution, and collect it in the intercellular spaces. In many plants it is found in such quantity that, by bursting the bark, it flows out in aqueous solution and dries, forming yellow transparent globules, as gum Arabic from different species of *Acacia*, cherry-tree and plum-tree gum. If the gum be a few times precipitated from the aqueous solution by alcohol, it is obtained pure. Entirely amorphous, transparent, of glassy fracture, inodorous, of insipid taste, very easily soluble in water, forming a thickish fluid or mucilage (emulsions, addition to ink). Insoluble in alcohol; is very easily converted into grape-sugar under co-operation of dilute acids (employment in medicine, as means of thickening).

3. Vegetable gluten. 3. *Vegetable Gluten*. It is as widely diffused as the gums. It is found in cells, partly deposited as a solid mass, and partly in a swollen condition. All

parts of plants, which contain gluten, form, when drenched with water, a thick, slimy mass, resembling paste; but no solution. Vegetable glutens appear to be combinations of gum with lime salts (phosphate of lime) and the difference between them is, probably, dependent upon the relative quantities of gum and salts of lime. If we digest the gluten with hydrochloric acid, entire solution follows, and, upon the addition of alcohol, pure gum is precipitated. Vegetable gluten, in common with gum and some starch, is found in tragacanth, cherry-tree and plum-tree gum, in buckthorn seed (*Trigonella fœnum Græcum*), in the seed of fleebane (*Plantago psyllium*), in linseed (*Linum usitatissimum*), in the bulbs of different species of *Orchis* (*salep*), in mallows, in root of *Althæa officinalis*, etc.

#### SPECIES OF SUGAR.

1. Milk-sugar. 1. *Milk-Sugar* (Lactin):  $C_{12}H_{22}O_{11} + 2aq.$  is found only in animal milk, and cannot yet be produced artificially from starch, dextrine, etc., although experience shows that milk-sugar is greatly increased in the milk by taking nourishment containing amyllum. The account is disputed that the milk of

bitches, restricted to carnivorous diet, contains no milk-sugar. Crystallizes in white quadrilateral columns, sharpened with two faces; hard, grates between the teeth, is dissolved in 6 parts cold water, and in from 3 to 4 parts of boiling, insoluble in alcohol and ether, tastes less sweet than the other sugar. By digestion with dilute sulphuric acid it is converted into grape-sugar; on the contrary, diastase and yeast do not appear to cause it to ferment; however, the Baschkirs and Kalmucks prepare an intoxicating drink (kumis), by fermentation of mare's milk. We obtain milk-sugar, by evaporating to syrup-thickness milk freed from the butter and cheese, the so-called whey.

2. *Cane-Sugar* (Common Sugar):  $C_{12}H_{22}O_{11} + aq.$  2. Cane-sugar. is found in sugar-cane, in sugar-maple (*Acer saccharinum*), and in other species of maple, in the red beet, and in the yellow, in several palms, in the nectar of flowers, etc., generally, inclosed in the cells in aqueous solution, with protein compounds and salts. Expressed sugar-juice soon commences fermentation at common temperature, because its protein substances change into ferment. Hence, in its production, care must be taken soon to remove these protein substances, which is done by boiling up the juice with 1-6th per cent. lime, straining and evaporating. The first crystals (muscovado) are purified by solution in water, treatment with animal charcoal and recrystallization, whereby, however, one part of the sugar is converted into uncrystallizable sugar, especially if the evaporation be carried forward at a high temperature. By slow evaporation of the pure sugar solution we obtain large, regular, well-formed crystals (rock-candy); if, on the contrary, the crystallization be interrupted by stirring, we obtain aggregated small white crystals (loaf sugar). Sugar is dissolved in almost all proportions in water (syrup), and is also dissolved, abundantly, by alcohol, proportionate to the water it contains. Of all sugars, the cane species is the sweetest; it is unchangeable in the air, and phosphoresces strongly when rubbed. In the heat, a solution of sugar is, by degrees, converted into uncrystallizable sugar, and in proportion as this occurs, the power of rotation of polarized light diminishes. In the presence of alkalies this change takes place slowly; on the contrary, very quickly under co-operation of acids. If the change has taken place, and the action continues, we obtain glucinic acid, humin substances, etc. If yeast be added to a solution of cane-sugar, fermentation soon commences, but previously the cane-sugar is converted into grape and uncrystallizable sugar. Cane-sugar melts at  $160^{\circ}$ , and stiffens to a translucent, uncrystallizable mass (barley sugar); at a high temperature it assumes a brown color (caramel).

3. *Fruit-Sugar*:  $C_{12}H_{22}O_{11} + x aq.$  3. Fruit-sugar. sweet fruits with grape-sugar. Honey is a mixture of fruit-sugar and grape-sugar. Fruit-sugar appears also to be

formed by the action of acids upon other sugars. It does not crystallize, tastes very sweet, is easily soluble in water and alcohol, loses its water entirely upon the water-bath. It absorbs water again in the air, and is said thus to be converted into grape-sugar. By the conversion of dextrine into grape-sugar, there is said to be formed, as middle member, uncrystallizable sugar, *Dextrin-Sugar*.

4. *Grape-sugar*. 4. *Grape-Sugar* (Starch Sugar, Granular Sugar):

$C_{12}H_{12}O_{12} + 2 \text{ aq.}$  Sweet fruit, as grapes, cherries, plums, figs, etc., also honey, contain fruit-sugar and grape-sugar. The separation of these is accomplished by alcohol, in which grape-sugar is not easily soluble. In the liver of different animals grape-sugar has also been found. If we digest starch (or dextrine, gum, cellulose), with 5 to 6 parts water and 2 to 3 parts sulphuric acid, it is entirely converted into grape-sugar; if the acid be removed by baryta, and the clear solution evaporated, we obtain the sugar in crystals. Diastase produces the same effect. In *diabetes mellitus* (saccharine urine), starch, cane-sugar, gum, etc., are converted into grape-sugar; this change commences even in the stomach; the grape-sugar is excreted in the urine; however, in many cases, crystallizable sugar is not formed. Pure grape-sugar is white, inodorous, grates between the teeth, is easily pulverized, tastes less sweet than cane-sugar, and crystallizes cauliflower-like, and in rhomboidal prisms. It is dissolved in 1 1-3 parts cold water, and in every proportion in boiling; insoluble in absolute alcohol, soluble in aqueous; at  $70^{\circ}$  it becomes soft, and at  $100^{\circ}$  it resembles a thick syrup; if a long time exposed to this temperature it loses 2 atoms water of crystallization. It is, like fruit-sugar, directly fermentable. With *chloride of sodium*, grape-sugar gives a colorless, rather hard combination, consisting of  $\text{NaCl} + 2(C_{12}H_{12}O_{12}) + 2\text{aq.}$ , which crystallizes in large, regular, hexagonal, double pyramids.

5. *Inosit*. 5. *Inosit*. In muscle, a sugar is found which quite agrees with grape-sugar, but in crystallized state contains two atoms more water.

### *Second Group.*

#### PECTIN-SUBSTANCES.

A few general properties.

The pectin-substances are allied to the carbohydrates in respect to their diffusion; they are found in almost all plants, especially in the fleshy fruits of the *Pomaceæ*, in very many roots, etc. They are not crystallizable; insoluble in alcohol; some are soluble, and some are insoluble in water; all possess the capability to form jellies with water; are in part neutral, in part acid. The original material from which the pectin-substances arise, *pectose*, is a body wholly inso-



luble in water. It is converted into the other pectin-substances by a ferment, pectase, occurring in fruits, as well as by boiling with water and dilute acids. They behave indifferent toward polarized light, and are not susceptible of being changed to sugar. Iodine does not act upon them. The constitution of pectose is unknown, because it cannot be separated from cellulose, without suffering a change. The constitution of the other pectin-substances and their compounds with oxide of lead, may be expressed by the following empirical formulæ:—

Pectose (?),		PbO.
Pectin,		
Parapectin,	$\left\{ \begin{array}{c} \text{C}_{64}\text{H}_{40}\text{O}_{56} + 8\text{HO} \end{array} \right\}$	$\text{C}_{64}\text{H}_{40}\text{O}_{56}, 7\text{HO}, \text{PbO. } 10 \text{ p. c.}$
Metapectin,	$\left\{ \begin{array}{c} \text{C}_{64}\text{H}_{40}\text{O}_{56} + 6\text{HO} \end{array} \right\}$	$\text{C}_{64}\text{H}_{40}\text{O}_{56}, 6\text{HO}, 2\text{PbO. } 19 \text{ p. c.}$
Pectosic acid,	$\text{C}_{32}\text{H}_{20}\text{O}_{28} + 3\text{HO} \dots$	$\text{C}_{32}\text{H}_{20}\text{O}_{28}, \text{HO}, 2\text{PbO. } 33.4 \text{ p. c.}$
Pectic “	$\text{C}_{32}\text{H}_{20}\text{O}_{28} + 2\text{HO} \dots$	$\text{C}_{32}\text{H}_{20}\text{O}_{28}, 2\text{PbO. } 33.8 \text{ p. c.}$
Parapectic “	$\text{C}_{24}\text{H}_{15}\text{O}_{21} + 2\text{HO} \dots$	$\text{C}_{24}\text{H}_{15}\text{O}_{21}, 2\text{PbO. } 40.8 \text{ p. c.}$
Metapectic “	$\text{C}_8\text{H}_5\text{O}_7 + 2\text{HO} \dots$	$\text{C}_8\text{H}_5\text{O}_7, 2\text{PbO. } 67.2 \text{ p. c.}$

If we commence at metapectic acid, the other pectin-substances appear as polymeric compounds of that acid. Probably pectose has a still higher constitution than pectin. The changes which take place in the conversions, consist, then, in a division into lower combinations of equal absolute constitution.

*Pectase* (Pectin Ferment): is obtained, if expressed Pectase.  
carrot-juice be precipitated by alcohol. The pectase soluble in water, is converted into an insoluble state by alcohol, without losing its action as ferment.

*Pectose* is found only in quite unripe fruit with Pectose.  
organic acids (citric and malic) and pectase.

*Pectin* occurs in fruits, which approach maturity; Pectin.  
it arises without doubt from pectose under the united action of pectase, heat and the acids occurring in unripe fruits. If we boil a crushed apple a short time, we obtain a gelatinous mass of pectin. In order to obtain it pure, apples or pears are expressed in the cold, the obtained juice filtered, the lime precipitated by oxalic acid, and the albumen by tannin. We filter again, and precipitate the pectin by alcohol. Pectin is also obtained when ground beets are heated, or treated with dilute acid. The gelatinous mass is washed with alcohol, then dissolved in cold water, and the pectin again precipitated by alcohol. White; soluble in water; is precipitated by alcohol from the concentrated solution in long threads, and from the dilute in the form of a jelly. Does not react acid, and gives no precipitate with a solution of sugar of lead. Alkaline bases with pectin immediately give pectic acid salts; under the influence of pectase, it is converted into pectosic acid; dilute acids convert it into pectic acid; by boiling with water, we obtain metapectin.



Parapectin.

*Parapectin.* We boil for a few hours a solution of pectin, and precipitate the parapectin by alcohol. Exactly resembles pectin; reacts neutral; gives a precipitate with a solution of acetate of lead; loses 2 atoms water at  $140^{\circ}$ .

Metapectin.

*Metapectin* is found in the over-ripe fruits, and is formed by boiling parapectin with a dilute acid. Resembles pectin, but reacts slightly acid, and gives a precipitate with chloride of barium, which is not the case with pectin and parapectin; in like manner it loses 2 atoms water at  $140^{\circ}$ . If metapectin be boiled with hydrochloric acid, we obtain, upon the addition of alcohol, a precipitate which contains hydrochloric acid.

Pectosic acid.

*Pectosic Acid.* We obtain this acid by the action of pectase upon a solution of pectin, likewise by the action of a cold dilute alkaline solution upon the same; from the alkaline fluid, acids precipitate the pectosic acid gelatinous; slightly soluble in cold water, soluble in boiling.

Pectic acid.

*Pectic Acid* is very easily formed if pectosic acid be boiled with water, also by the action of acids, or an excess of alkaline bases upon pectin. We generally obtain the acid by boiling expressed beet-juice with a solution of pure potassa; we filter, precipitate the acid with chloride of calcium, decompose the precipitate with hydrochloric acid, and wash the deposited pectic acid with water. Insoluble in cold water, slightly soluble in boiling. But if we boil pectic acid a long time with water, it is completely dissolved under the formation of parapectic acid. It is gelatinous, and gives, with alkalis, easily soluble uncrystallizable compounds. If an excess of base be present, the pectic acid is soon changed into metapectic acid. The warm solution of the neutral alkali salt gelatinizes by cooling; with the earthy and metallic salts it gives gelatinous precipitates. By the action of dilute *nitric acid* upon *woody fibre*, we obtain an acid which has the greatest similarity to pectic acid, with which it seems to be identical.

Parapectic acid.

*Parapectic Acid* is formed by boiling pectic acid with water; the pectic acid salts at  $150^{\circ}$ , and by boiling with water, are converted into parapectates. Easily soluble in water, reacts strongly acid. The alkali salts are soluble; with baryta water, in excess, an insoluble compound arises.

*Metapectic Acid.* Its production is already given; it is best obtained if pectic acid be boiled several days with water; parapectic acid is very soon converted into metapectic acid. Soluble in water, and with all bases gives salts soluble in water; by excess of base, the salts assume a yellow color in the air. Is found in over-ripe fruit.

Pyropectic acid.

*Pyropectic Acid:*  $C_{14}H_9O_9$ , is formed with carbonic acid and water, if pectin or metapectin be exposed to a temperature of  $200^{\circ}$ . Black, insoluble in water, forms, with the alkalis, uncrystallizable combinations.

As is well known, many fruits ripen afterwards if taken unripe from the tree. As remarked, only <sup>Ripening of fruit.</sup> pectose occurs in the unripe fruit; by ripening, pectin and parapectin arise, and by over-ripening, metapectinic acid is formed, which may contribute to the changing of starch into sugar. The change, therefore, in the consistence of the fruit, depends not upon cellulose, but upon pectose. The unripe, green fruit emits oxygen in the light; by ripening, the green coloring-matter vanishes, and now an emission of carbonic acid takes place by day. If we spread air-tight varnish over unripe fruit, the ripening is prevented, because, without doubt, the exchange of gases cannot now take place. In proportion as the pectose changes, sugar is produced; pectose, however, is not converted into sugar. The latter arises, probably, by the action of the acids present upon starch and vegetable gluten. In proportion as the ripening progresses, the acids are saturated with bases, as with potassa and lime.

## 2. Nitrogenous Combinations.

To the nitrogenous compounds belong:—

- a. *The Protein-Substances.*
- b. *The Membranes, giving Glue and Chondrin, and*
- c. *The Animal Coloring Matters.*

The most important combinations, of which the organic structure of the animal organism consists, and which form the principal mass of animal bodies, are protein substances, and the membranes giving glue and chondrin. The latter are insoluble in water, but if they are a long time boiled with water entire solution follows, and, by cooling, the entire solution stiffens to a jelly (glue); by this conversion into glue the membranes appear to suffer no change in their constitution, and the change may be compared to that of starch into the like constituted dextrin. The protein-substances, on the contrary, are quite decomposed by boiling with water; they form, in part, substances soluble in water, but which do not gelatinize by cooling.

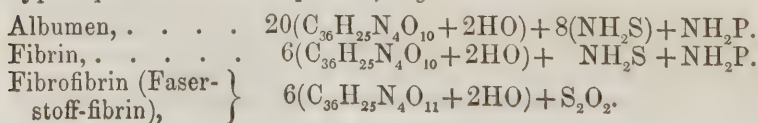
### *First Group.*

#### PROTEIN-SUBSTANCES.

Organic combinations, which are classed with the protein compounds, are found not alone in the animal organism, but also in the vegetable kingdom; and it has been already remarked, in the General Part, that all <sup>Constitution of the protein-substances.</sup>

materials which are necessary to the nourishment of animal bodies, and from which animal structures are produced, occur in organized form in the vegetable kingdom. But it is not yet strictly proved that the vegetable compounds are perfectly identical with those of the animal kingdom. Physically, this is decidedly not the case; the animal substances appear to be richer, also, in oxygen, than the vegetable. Indeed, it is doubtful whether the constitution of the substances belonging to the protein combinations is the same, and the numerous analyses presented have not been able to determine the question because of the fact, that, as yet, we are unable to ascertain the purity of the above-mentioned substances, and very often the elementary analyses have been undertaken with mixed materials. Nevertheless, these substances present, in a chemical view, so many common relations, that they, like the carbohydrates, may be considered a distinct class of organic compounds. Besides carbon, hydrogen, nitrogen, oxygen, and a few salts, the protein combinations contain, also, a small quantity of sulphur and phosphorus. In what form these elements therein appear, whether as elements united directly with the other elements, or not so united, is, likewise, not yet ascertained. If we dissolve the protein substances in Protein.

potash lye by gentle heat, and cautiously saturate the solution with acetic acid, a gelatinous precipitate is produced, whose proportions are the same, whether we have used one or another of the protein substances for the research, and in the solution is found sulphide of potassium, and traces of hypophosphite of potash. This behavior has led to the supposition that in all protein substances consisting of nitrogen, carbon, hydrogen, and oxygen, a common body exists, to which we have given the name *Protein* (from *πρωτεῖνω*—*I take the first place*), and we seek to explain the difference in the protein compounds, by considering them as combinations of protein with different quantities of phosphorus and sulphur. From the elementary analyses of protein, we calculate the following formula:  $N_{50}C_{400}H_{310}O_{120}$ , with which 1 and 2 atoms of sulphur and phosphorus are believed to occur in the protein combinations. Yet, since it is proved that protein is not a *non-sulphurous* substance, this opinion can no longer be sustained, and whilst people cannot divest themselves of the idea of a *protein*, in order to maintain this idea, they arrive at other strange and truly novel opinions. They now suppose various compounds of protein; a few of these are said to consist of protein +  $NH_2S$ , and  $NH_2P$ ; others are said to be constituted of hyposulphurous acid and protein, *e. g.*



If we dissolve fibrin in dilute potash lye, and precipitate with acetic acid, the precipitate is said to be fibrofibrin (*Faserstoff-fibrin*). As an especial fundamental compound, as little can be said of protein matter in the sense of *protein*, as of the carbohydrates. Since these latter must be considered as different compounds, notwithstanding their similarity of constitution, and as starch is not dextrine, and dextrine is not sugar, with like reasoning albumen is not fibrin, and casein is not legumin. The protein compounds, even if their similar constitution shall be hereafter more certainly proved to differ physically, must be viewed as accordant with each other in the common chemical relations. It has already been shown in reference to the carbohydrates that rational formulæ could not be determined. That, on the contrary, the empirical formulæ, from several fixed compounds which they form, may be ascertained with much probability. With the protein-substances, it is as yet clearly impossible to determine even an empirical formula with but an approximation to correctness, not alone on account of the difficulty mentioned, of obtaining them in a pure form, but also on account of the want of positive compounds of the same, and because of the ease with which they decompose. From the analytical results presented, the most different formulæ may be calculated with equal probability. There are, indeed, compounds of higher order, whose proximate and remote constituents unite but slightly with each other, hence their great inclination to decomposition, and to fall into compounds of a lower order. Many of the phenomena of decomposition make it in a certain degree probable that they produce compounds of the carbohydrates with nitrogenous bodies. In the present state of our knowledge in respect to these bodies, we must abandon every formula by which their atomic constitution is said to be expressed. Generally, they contain in 100 parts: 55.16 carbon, 7.05 hydrogen, 21.81 oxygen, 15.96 nitrogen, with  $\frac{1}{2}$  to 1 per cent. sulphur and phosphorus in an unknown form.

The protein compounds do not possess the property of crystallizing; they are tasteless and in-  
 odorous; insoluble in alcohol and ether, and in part  
 soluble in water. If dried in gentle heat, they  
 appear brittle and transparent. When moist and fresh, they are  
 often gelatinous, and then contain a great quantity of water.  
 They are known in two modifications—in the fresh  
 state, and in the coagulated. Heat, boiling water,  
 alcohol, and mineral acids, conduct them from the  
 fresh into the coagulated modification; in the latter,  
 the compounds are insoluble in water, more permanent, and less  
 subject to spontaneous decomposition. None of them are volatile,

Common chemical properties of the protein-substances.

Different states of protein-substances.



Behavior to heat.

as the conditions

Products of putrefaction.

Behavior by boiling with water.

powder.

Behavior to oxidizing bodies.

Behavior to chlorine and hydrochloric acid.

Behavior to acids.

and, by dry distillation, they give the products mentioned page 50. For the phenomena which were observed in the putrefaction of protein-matter, as well as the conditions under which these occur, see page 52. As products of putrefaction, may be mentioned the carbonate, acetate, butyrate, valerianate, capronate, etc., of ammonia; also leucin, tyrosin, etc.

If the protein-substances be long boiled with water, there is formed some carbonate of ammonia, various substances soluble in water, whilst the remaining undissolved part may be at last ground to powder. Hence oxygen must be absorbed, and, according to the theory of protein, it must be more highly oxidized, forming *bioxide* and *trioxide* of protein.

When heated a long time with *peroxide of manganese*, and *dilute sulphuric* or *chromic acid*, the protein-substances give all the acids of the formyl series up to caprylic acid, as well as the nitryls of the same, particularly nitrovaleryl, oil of bitter almonds, benzoic and hydrocyanic acid. If they are heated with *concentrated nitric acid*, they become yellow—(*xanthoproteinic acid*). A solution of *nitrous acid*, in *nitrate of protoxide of mercury*, imparts an intense red color to the protein compounds.

If into a solution of protein-substances *chlorine* be conducted, white flakes, containing chlorine, are formed. These are said to consist of protein-substances and chlorous acid. These compounds must give trioxyprotein by the action of ammonia. By *concentrated hydrochloric acid*, the protein-substances, when gently heated in the air, are colored intensely blue, and in part dissolved with blue color; however, only under decomposition.

*Acetic* and a few other *organic acids*, likewise *common phosphoric* and *dilute hydrochloric acid*, dissolve the protein compounds without decomposition, both in their soluble and in their insoluble modification. *Ferrocyanide of potassium* produces a white precipitate in the solution, and *ferricyanide of potassium* a lemon-yellow one; both of these dissolve in potassa, under production of ferrocyanide of potassium.

In *concentrated mineral acids* the protein-substances are insoluble. They swell gelatinous in the acids with which they combine. These compounds are insoluble in acidulated water; when perfectly washed, on the contrary, they easily dissolve in pure water; but there probably exist no definite compounds with acids. If we let *hydrate of sulphuric acid* act a long time upon them, they are decomposed under production of leucin, tyrosin, and humus-like substances. All protein combinations are precipitated by *tannin* from their solution.

*Solutions of pure alkalies* completely dissolve the protein compounds, particularly in the heat; acids, however, as already remarked, again precipitate them no longer unchanged from their solutions. If we mix them with alcohol, precipitates are formed, which are alkaline. By heating the solution, it evolves ammonia. If we boil the protein compounds a long time with concentrated potash lye, complete decomposition takes place under evolution of carbonate of ammonia and production of leucin, glycocoll, and different acids. If to a solution of protein-substances in acetic acid we bring different metallic salts, precipitates are formed consisting of metallic oxide and protein-substance.

Behavior to bases.

If to a solution of albumen we add a solution of metallic salts, as sulphate of copper, nitrate of silver, bichloride of mercury, etc., precipitates are formed, which consist of albumen-metaloxyd and of the compound of albumen with the acids. The latter can be removed with water, whilst the albumen-metaloxyd remains undissolved. (Use of protein-substances, as albumen and casein in metallic poisoning.)

Behavior to salts.

#### PROTEIN COMBINATIONS OF THE VEGETABLE KINGDOM.

1. *Legumin* is found, in common with starch, in the leguminous plants, as the bean, the pea, and the lintel. By soaking these, legumin is dissolved and is precipitated from the solution by acetic acid and purified by washing with alcohol. Freshly precipitated, it appears in white flakes of mother-of-pearl lustre; dried, it possesses a yellow color, and is easily ground. The aqueous solution is coagulated like albumen; acetic and phosphoric acid precipitate it from the solution, but it easily dissolves in an excess of acetic acid. Rennet also causes it to coagulate. Gives no soluble compound with carbonate of baryta. In the seeds which afford oil, a nitrogenous body is found, which appears to be identical with legumin. In them is found still another nitrogenous substance, which is called *emulsin*, or *synaptase*, but varies from the protein-substances in constitution; under its action amygdalin decomposes into hydrocyanic acid, oil of bitter-almonds and sugar, and salacin into sugar and salagenin (p. 56). A quite similar body is *myrosin*, which occurs in black mustard (p. 428).

1. Legumin.

Synaptase.

Myrosin.

2. *Vegetable Gluten*. If meal of the grains be kneaded in a linen cloth with water, until the latter takes up no more starch, there remains in the cloth a gray, elastic, tasteless mass, which consists of coagulated albumen and vegetable gluten. The latter is soluble in boiling alcohol, and is precipitated in flakes during the cooling; thereby vegetable

2. Vegetable gluten.

gluten differs from the other protein compounds. In moist condition it has a yellow color, may be drawn out between the fingers, is adhesive, tasteless, and causes meal, when stirred with cold water, to give a paste. Dried, it is yellowish, transparent, horn-like, and pulverizable. Insoluble in water.

3. *Vegetable Albumen* appears not to be different from animal albumen. Is found in almost all vegetable juices; if these are heated to boiling it is coagulated. Also in the *yeast cells* is found, dissolved, a protein compound, which is, probably, albumen.

#### PROTEIN COMBINATIONS OF THE ANIMAL KINGDOM.

1. *Soluble albumen.* 1. *Albumen* is much diffused in the animal body. It is the principal constituent of blood, is found in eggs of birds, of lizards, of fish, in lymph, in chyle, in different serous secretions, as in pus, in the dropsical, and many other pathological fluids, mostly in combination with soda. If blood be left at rest, it separates into the coagulum and the serum. The latter is a solution of different salts and of albumen-soda in water. If the serum be evaporated at the temperature of  $50^{\circ}$ , and the dry residue washed out with ether and alcohol, there remains an amber-yellow mass, which is mostly dissolved in water; the solution contains most all salts, besides a portion of albumen; the residue is nearly pure albumen, which is soluble, of course, in pure water. In dry condition it is pulverizable, and may be heated to  $100^{\circ}$  without losing its solubility. The solution coagulates completely at  $63^{\circ}$ . Alcohol, creosote, and acids (except acetic), cause it to coagulate. Rennet is without action.

*Coagulated Albumen.* We obtain coagulated albumen pure, if we precipitate a solution of albumen by hydrochloric acid, dissolve the precipitate after washing in pure water, reprecipitate the albumen by carbonate of ammonia, and extract it by alcohol and ether. It shows all the properties above mentioned. If we dissolve coagulated albumen in dilute potash lye, digest the solution some time at  $60^{\circ}$  to  $70^{\circ}$ , and then precipitate with acetic acid, we obtain a snow-white, flocculent precipitate, which contains less sulphur than common albumen; the sulphur can no longer be detected by the ordinary reagents. If it be fused with caustic alkalies, however, it forms sulphide of potassium. The albumen thus obtained is said to be a compound of protein with  $S_2O_2$ .

2. *Fibrin.*

2. *Fibrin.* Fibrin is found dissolved in the blood during its circulation, in chyle, in lymph. In coagulated state it forms the principal constituent of the muscles. If the blood be withdrawn from the living body, the fibrin separates,

at first, in fine threads, which soon contract to a coherent, elastic mass, in which the coagulation of the blood consists. The crassamentum which forms when blood is left at rest, is fibrin, which the blood-corpuscles inclose, pervaded by serum. The coagulation of dissolved fibrin is accelerated by exposure to the air. By the addition of the alkali salts, as well as by shaking with carbonic acid, the process is retarded.

*Coagulated Fibrin.* It is obtained, if freshly-  
 drawn blood be gently stirred with a twirling stick. Coagulated fibrin.  
 The fibrin which adheres to the stick is washed with distilled water until it appears white. In moist condition it possesses the capability of rapidly decomposing deutoxide of hydrogen. Dried, it appears as a yellowish, opaque, hard, brittle, tasteless, and inodorous mass; in water it swells up, and again acquires its former properties. In fresh condition it is easily dissolved in acetic acid and in alkalis, and very soon commences to putrefy. If it be digested in a solution of nitrate of potassa (3 parts nitrate of potash and 50 parts water), it is thus completely dissolved; by heating, the solution coagulates like albumen. Other alkali salts also dissolve fibrin. Fibrin is richer in oxygen than albumen. If we bring, spontaneously coagulated fibrin a few minutes into boiling water, it assumes all the Dried fibrin. properties of albumen, is then no longer soluble in aqueous nitrate of potash, and no longer possesses the capability to decompose deutoxide of hydrogen. By oxidation with peroxide of manganese and sulphuric acid, fibrin is said to give more butyric acid than do the other protein compounds, but less acetic and benzoic acid. If fibrin be dissolved in very Bioxypotein. dilute potash lye, and precipitated with acetic acid, we obtain a light yellow precipitate, which dries to a brownish-green resinous mass. This is pasty in warm water, and may then be drawn out in threads. The same substance is said, also, to be obtained if fibrin be a long time boiled in water, exposed to the air, as well as by dissolving hair or horn in potash lye, and precipitating by acetic acid. This body is the so-called fibrin-protein, or bioxypotein, as it was formerly called; it is said to be a compound of oxyprotein with  $S_2O_2$ .

If we boil fibrin, albumen, or casein, a long time Trioxyprotein. with water, with access of air, evaporate the solution, and extract the residue with alcohol, a body remains, which, by drying, becomes brittle, is dissolved in cold water, and precipitated from the solution by mineral acids, and by metallic salts, but not by ferrocyanide of potassium. This body is said to be still richer than the former in oxygen, and to exhibit a combination of oxidized protein with  $NH_4O + 3HO$ , therefore, of oxide of ammonium with water (?). The same substance must also be found in inflamed blood, in pus and in pathological tumors; it must



farther be obtained by decomposition of the so-called chlorite of protein with ammonia. If we dissolve this body in alkalies, and precipitate it with an acid, the true trioxypotein must be precipitated.

Vitellin.

*Vitellin.* If we stir the yolk of egg with water to an emulsion, we obtain, after the fat is separated, a solution which, at  $75^{\circ}$ , coagulates like albumen, but is not precipitated by copper and lead salts. The coagulated vitellin behaves quite like coagulated albumen, but contains more oxygen.

3. Casein.

3. *Casein* (Caseum) is said to contain no phosphorus, and is thereby distinguished from the other protein combinations. It is the protein compound of animal milk, and is known in a soluble modification, and in an insoluble. Fresh milk is precipitated by dilute sulphuric acid, and the washed precipitate is dissolved in carbonate of soda. The solution is left standing, at  $20^{\circ}$ , until the fat separates, and is then again precipitated by an acid. From the precipitated casein the adhering acid, as well as the fat, is withdrawn by long treatment, first with water, then with alcohol and ether. The casein thus obtained exhibits, after drying, a transparent amber-yellow mass, which is slightly soluble in water, but easily soluble if the water contains a little free potassa. This alkaline solution does not coagulate by heating; by evaporation upon the water-bath, a film of coagulated casein rises upon the surface. From the solution the casein is precipitated by acids, even by acetic acid, without perceptibly dissolving in excess, but it is easily dissolved in oxalic and tartaric acid. Gives, not with potassa alone, but also with lime and baryta, combinations soluble in water. The ash of casein contains much phosphate of potassa and of lime.

Coagulated casein.

*Coagulated Casein* (Cheese). If a solution of casein, or fresh milk, be gently heated with the mucous membrane of the stomach of a young calf, the so-called rennet, the casein is completely coagulated, and forms a coherent, quivering jelly. One part rennet is sufficient to coagulate 1800 parts milk. In dry condition, coagulated casein appears as a transparent, hard, yellowish mass, which is insoluble in water, and behaves almost exactly like coagulated albumen. It is not easily soluble in acetic acid; by heating with potash lye it evolves sulphide of ammonium. Fused with hydrate of potassa, we obtain leucin, tyrosin, and valerianic acid, under evolution of hydrogen gas.

4. Crystallin.

4. *Crystallin* is the protein compound of the crystalline humor of the eye. In order to obtain it, the crystalline lens is washed with water, ground, and then mixed with water and filtered. The solution coagulates like albumen, by heating, and generally agrees in most properties with a solution of the latter substance. In dry condition it is completely white and

pulverizable. If we accurately saturate the acetic acid solution with ammonia it is precipitated. Crystallin is said to contain no phosphorus. In the red blood corpuscles a fluid is found inclosed which consists of the coloring matter of the blood and a protein compound. This fluid is said to be identical with crystallin; according to other accounts, it is a special protein combination, which has been called *globulin*. Globulin.

5. *Horn-Tissues*. To the *horn-tissues* belong hair, nails, horn, claws, and farther, the epidermis and epithelium. These substances dissolve completely by boiling with potash; upon the addition of acids a lively evolution of hydrosulphuric acid follows; hair contains 5 per cent. of sulphur. Horn structure.

*Fibroin*:  $N_{6.33}C_{39}H_{31}O_{17}(?)$ . We obtain this substance if raw silk or gossamer be successively boiled in alcohol, water, and acetic acid, and the residue again boiled with water until it no longer reacts acid. Appendix to the protein compounds. It is white, elastic, insoluble in acetic acid; it dissolves in hydrochloric and concentrated sulphuric acid, and is precipitated from its solution by tannin. Soluble in strong potassa solution, and again precipitable, unchanged, by dilution with water. The principal part of the sponge is said to be a combination of fibroin with iodine, sulphur, and phosphorus.

*Chitin*:  $N_{6.33}C_{46.69}H_{67.69}O_{40.89}$  is the horny substance of the articulata; it is obtained if the sheath, wings, and shields of the beetle, the shell of the crab, of the lobster, spider, etc., be successively extracted with water, alcohol, ether, and dilute potassa solution. It is white, and of the form of the original tissue. Is dissolved in hydrochloric and in nitric acid without change of color. Drenched in concentrated sulphuric acid, it swells up and liquefies without blackening. Insoluble in concentrated potassa solution. Chitin.

### Second Group.

## TISSUES AFFORDING GLUE AND CHONDRIN.

### GLUE AND CHONDRIN.

The tissues which furnish glue and chondrin are found only in animal bodies. To these belong all parts of the animal organism formed of ligamentous tissue, as the tendons, ligaments, fasciæ, the fibrous tissue, the true skin, the cartilaginous tissue, and, in part, the elastic tissues. These substances are insoluble in water. The ligamentous tissue swells up in acetic acid; the cartilaginous tissue, as well as the fibres of the elastic tissues, do not change in acetic Tissue giving glue and chondrin.

Leather. acid. In moist condition these bodies easily putrefy.

If the tissues from which glue is obtained are brought into a solution of tannin, they absorb the latter completely, and give therewith a coherent compound—leather, which resists putrefaction and is perfectly insoluble in water. Leather is obtained if the fresh, carefully cleaned, animal skins be brought in contact with bodies containing tannin under exclusion of air.

If the above-mentioned substances be boiled a long time with water, they are dissolved, and change into glue, which, however, possesses different properties, according to the substance from which it is obtained. That procured from ligamentous tissue and from the cartilaginous basis of bones, is *ordinary glue*, and that from permanent cartilage, with the exception of the glue from fibrous cartilage, is called *chondrin*. It differs from the protein substances in this, that it is not precipitated by ferrocyanide of potassium from the acetic acid solution; assumes no blue color by hydrochloric acid, and no yellow by nitric acid. But if it be treated with peroxide of manganese and dilute sulphuric acid, or with chromic acid, it thus gives the same products as protein substances; in the same manner as by the action of nitric acid, hydrate of potassa, and hydrate of sulphuric acid.

#### 1. Glue.

1. *Glue* (Bone Glue):  $\text{N}_2\text{C}_{13}\text{H}_{10}\text{O}_5$  (?) : is obtained very pure, if from the cleansed bone the phosphate of lime be withdrawn by digestion with dilute hydrochloric acid and the cartilaginous substance, which remains after the requisite washing be changed into glue by boiling with water. The obtained solution is so far evaporated that it stiffens by cooling. The jelly is then cut in thin slices and dried by gentle heat. In the bladder of the sturgeon, glue appears to occur ready formed. Colorless, transparent, hard, tasteless, and inodorous mass; reacting neutral. Softens in cold water, in which it dilates, becomes opaque, and, by gentle heating, completely dissolves, forming a clear colorless fluid, which, by cooling, stiffens to a clear jelly. Insoluble in alcohol, ether, fats, and volatile oils. If glue be often dissolved in warm water, it thus loses the capability of gelatinizing, which appears to be caused by absorption of water. If *chlorine* be conducted into a solution of glue, a white elastic foam is formed, which is said to consist of glue and chlorous acid. Dilute, pure *alkalies* and *ammonia* do not deprive glue of the property of gelatinizing; but if the solution be accurately saturated with acetic acid and then evaporated, it no longer gelatinizes. *Alum* and *sulphate of alumina* produce no precipitate in the solution; with a mixture of *common salt* and *alum*, on the contrary, a white precipitate is formed. *Sulphate of peroxide of iron* produces no precipitation in the cold, but by boiling a precipitate is formed, which is said to consist of 1 atom of glue and 1 atom of sexa-sulphate of peroxide of iron. *Protochloride of tin*, *neutral* and *basic acetate of lead*,

bichloride of mercury, sulphate, of platinum, and chloride of platinum cause a precipitation.

2. *Chondrin* (Cartilage Glue):  $N_4C_{32}H_{26}O_{14}$  (?), is 2. Chondrin. obtained by boiling the permanent cartilages (except fibrous cartilages). Quite resembles glue, yet *alum* and *sulphate of alumina* precipitate chondrin from its solution, in white compact flakes. *Acetic acid* produces turbidity, which does not vanish by the addition of much acid; *sulphate of peroxide of iron* immediately occasions a copious precipitate, which is soluble in an excess of the precipitant. Chondrin contains a small quantity of sulphur.

### Third Group.

#### ANIMAL COLORING MATTERS.

*Hæmatin* (Coloring Matter of the Blood):  $N_3C_{44}H_{22}O_6Fe$  (?). Coloring matters of the blood. *Hæmatin*. Hæmatin is found intimately combined with a protein compound (globulin) in the blood corpuscles. If we mix freshly drawn blood with a concentrated solution of sulphate of soda, the blood corpuscles separate, whilst albumen and fibrin remain dissolved. The corpuscles are collected upon a filter, and boiled out with alcohol and a little sulphuric acid. The filtered solution is saturated with carbonate of ammonia, and the solution of hæmatein-ammonia filtered from the sulphate of ammonia is evaporated; as residue, hæmatin remains, which is freed from fat by ether. Brownish-black; tasteless, and inodorous powder; insoluble in water, alcohol, ether, fats, and volatile oils. It burns without fusion; evolves thereby an odor like burnt horn, and leaves behind pure oxide of iron. *Nitric acid* completely destroys hæmatin by boiling. If hæmatin be shaken with *chlorine water*, the color vanishes instantly; white flakes are formed, and in the abfiltered fluid hydrochloric acid and perchloride of iron are found. If *hydrate of sulphuric acid* act a long time upon hæmatin, we obtain, under evolution of hydrogen gas (?), hæmatin free from iron, but still red. With *mineral acids* hæmatin forms combinations insoluble in water, but soluble in alcohol. The compounds with the *alkalies* are dissolved in water with dark blood-red color; they are also soluble in alcohol and ether. If the solution of hæmatin, in slightly alkaline water, be accurately saturated with acetic acid, we thus obtain a reddish-brown fluid, in which neutral and basic acetate of lead, acetate of copper, and nitrate of silver produce green and brown precipitates; ferrocyanide of potassium produces no precipitation.

*Hæmaphæin*. This yet little known coloring matter is said to be found, in small quantity, in arterial 2. Hæmaphæin.



as well as in venous blood, and to determine the yellow color of the serum. It differs from hæmatin in its solubility in water, alcohol, and ether. In the blood of *Malæna* this coloring matter is said to occur in large quantity; it is, without doubt, a product of the decomposition of hæmatin.

3. Hæmatoidin. *Hæmatoidin*. In ligatured bloodvessels and in extravasation, are found small crystals, sometimes yellow, sometimes red, which are insoluble in water, alcohol, ether, acetic acid, in dilute mineral acids, and in dilute alkalies; they are called hæmatoidin, and do not always appear to contain iron.

*Pigmentum nigrum oculi* (Augenschwarz), is found, mixed with mucus (schleim), in the eye of man and of the inferior animals. In order to obtain it, the choroïdea of the ox, bearing the *Pigmentum nigrum*, is taken out, prepared, and laid in pure water until the latter is no longer colored. The pigment is then stripped off with a hair pencil under water. A black, dull-looking, inodorous, and tasteless powder, which is dissolved in pure potassa in the heat, under evolution of ammonia. It is a mixture of different substances. The so-called ink of the cuttlefish (genus *Sepia*) is a similar coloring matter.

Coloring mat- *Gall-Brown* (Cholepyrrhin). The color of the  
ters of the gall. gall is due to a brownish-yellow coloring matter,  
Gall-brown. which, however, cannot be separated from the gall  
without decomposition. If a fluid containing this

coloring matter be, by degrees, mixed with nitric acid, it assumes, successively, a brownish, green, violet, red, and at last, yellow color. This substance is occasionally found, as a muddy deposit, in the gall, or collected as a concretion, forming gall-stones, which show the above-mentioned reaction with nitric acid. It possesses a yellow, or reddish-brown color, is infusible, tasteless, and inodorous, insoluble in water. Dissolves in potassa, with yellow color; the solution assumes a green color in the air, under pro-  
duction of leaf-green. The so-called *gall-yellow*

Gall-yellow. (Bilifulvin, Bilifulvinic Acid) arises, probably, from  
gall-brown. Also in *urine* are found several *color-*  
Coloring mat-  
ters of urine. *ing matters*, whose nature, however, is not yet known.

## SEVENTH DIVISION.

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### GENERAL PRODUCTS OF THE DECOMPOSITION OF PROXIMATE CONSTITUENTS OF THE VEGETABLE AND OF THE ANIMAL KINGDOM.

#### ULMIN-SUBSTANCES AND HUMIN-SUBSTANCES.

By mouldering and putrefaction (p. 57), the common constituents of plants and animals separate into a series of substances, which are distinguished by fixed durability, and are called ulmin and humin substances. The same matters are obtained by the action of acids and alkalies upon the above compounds. By mould, is understood that mixture of the products of decomposition with disintegrated rock which covers the surface of the earth, whose fertility is mainly dependent upon the organic products of decomposition. As the process of decay does not cease, the organic constituents are subject to a constant change; thus, by the oxidation of ulmic acid arises humic acid, from humic acid geïc acid, and, in like manner, by the oxidation of geïc acid, crenic acid may be formed. In the soil, the above-mentioned acids are generally united with bases, especially with ammonia. The constitution of these matters is expressed by the following empirical formulæ:—

Ulmin . . . . .	$C_{40}H_{16}O_{14}$
Ulmic acid . . . . .	$C_{40}H_{14}O_{12}$
Humin . . . . .	$C_{40}H_{15}O_{15}$
Humic acid . . . . .	$C_{40}H_{12}O_{12}$
Geïc acid . . . . .	$C_{40}H_{12}O_{14}$
Crenic acid (Quellsäure) . .	$C_{24}H_{15}O_{19}$
Apocrenic acid (Quellsatzsäure)	$C_{48}H_{22}O_{24}$

Of these substances, crenic acid is soluble in water, apocrenic, ulmic, and humic acid dissolve in alkalies; ulmin and humin are insoluble in water and in alkalies; but to a certain extent, they can be made soluble by being changed into ulmic and humic acid. These compounds are all amorphous and inodorous. If

they be fused with hydrate of potassa, with evolution of hydrogen gas, we obtain formic and carbonic acid. They are decomposed by nitric acid, and, with chlorine, they give various chlorine-products.

Under *ulmin-substances* are generally included the matters which are formed by the action of acids upon sugars, as well as each of those which occur in nature in some kinds of brown turf. In constitution, these matters agree with each other, but in their remaining relations they show such marked deviations, that they cannot be considered as identical. They are of brown color, and are led over, by the action of acids, under absorption of oxygen, into the humin-substances. If we treat cane-sugar a long time with a dilute acid, below the boiling point, it forms brown flakes; if we treat these with alkalis, ulmic acid is dissolved whilst ulmin remains.

1. Ulmic acid. *Ulmic Acid* is precipitated from the alkaline solution by an acid, as a brownish jelly, which completely dissolves in water. By being well dried, it loses its solubility. The solution of ulmate of ammonia gives, with the metal salts, precipitates which consist of ulmate of ammonia and ulmates of metals.

2. Ulmin. *Ulmin*. A brown substance, insoluble in water, acids, and alkalis. After a long time, ulmin is changed, by alkalis, into ulmic acid.

In relation to the *Humin-substances*, in general, the same is true that is given in connection with the ulmin-substances. They all naturally contain water and ammonia in various proportions; they occur in black turfs, in soil, and in soot; they essentially differ from the artificial, and have different atomic weights.

*Humic Acid*. If we boil a long time 8 parts sugar with 2 parts concentrated hydrochloric acid and 20 parts water, we obtain a dark-brown body—a humin-substance. This is treated with potassa, and the humic acid precipitated by hydrochloric acid. It appears a blackish-brown, slippery mass, of slightly astringent and acid taste. When dry it is black, inodorous, and tasteless. With the alkalis, it gives soluble compounds; with the alkali earths and heavy-metal oxides, sometimes soluble, sometimes insoluble compounds. Humic acid has a great tendency to absorb ammonia, and holds it so firmly that, even by boiling with carbonate of soda, it does not escape.

By absorbing oxygen, humic acid is converted into *geïc acid*. If we extract soil with carbonate of soda, and precipitate with hydrochloric acid, the precipitated humic acid contains, also, ammonia.

*Humin.* The portion of humin-substance, which is insoluble in alkalies, is dark-colored, and is converted, by the influence of strong alkalies into humic acid.

Humin.

*Crenic and Apocrenic Acid* (Quellsäure and Quellsatzsäure). These acids are found in the water of several springs, and appear to be common products of putrefaction; they are found in soil, in mouldering wood, in brown iron-stone (ore), in iron-ochres, etc.

Crenic and apocrenic acid. Their formation.

Apocrenic acid is formed by the action of nitric acid upon ulmin-substances and humin-substances, and appear also to be formed by the action of that acid upon crude iron. The pure acids are non-nitrogenous, but generally the acids contain ammonia. They are best obtained from ochre, which is boiled with caustic lye. The alkaline fluid, over-saturated by acetic acid, is mixed with acetate of copper as long as a precipitate is formed of apocrenate of copper. From the solution, crenate of copper is precipitated by carbonate of ammonia. In the decomposition of metallic salts by hydrosulphuric acid, we obtain the pure acids, which, however, as remarked, contain ammonia.

*Crenic Acid* (Quellsäure) appears as a hard, transparent, sulphur-yellow, inodorous mass; not crystalline; soluble in all proportions, in water and in alcohol; of a taste at first sour, and afterwards astringent. By heating with pure potassa, it evolves ammonia. By long standing in the air, it is converted into apocrenic acid. It forms with bases yellow compounds, some of which are soluble and some insoluble. The salt of protoxide of iron is found in several mineral waters. But these salts all contain ammonia, and are to be considered as double salts.

1. Crenic acid.

*Apocrenic Acid* (Quellsatzsäure) possesses a dark color; is soluble in water and alcohol; reddens litmus; tastes not sour, but astringent like tannin. From the solution in water, the acid is precipitated by hydrochloric acid. The salts possess a dark color; they agree in solubility with the crenic acids; they all contain ammonia.

2. Apocrenic acid.

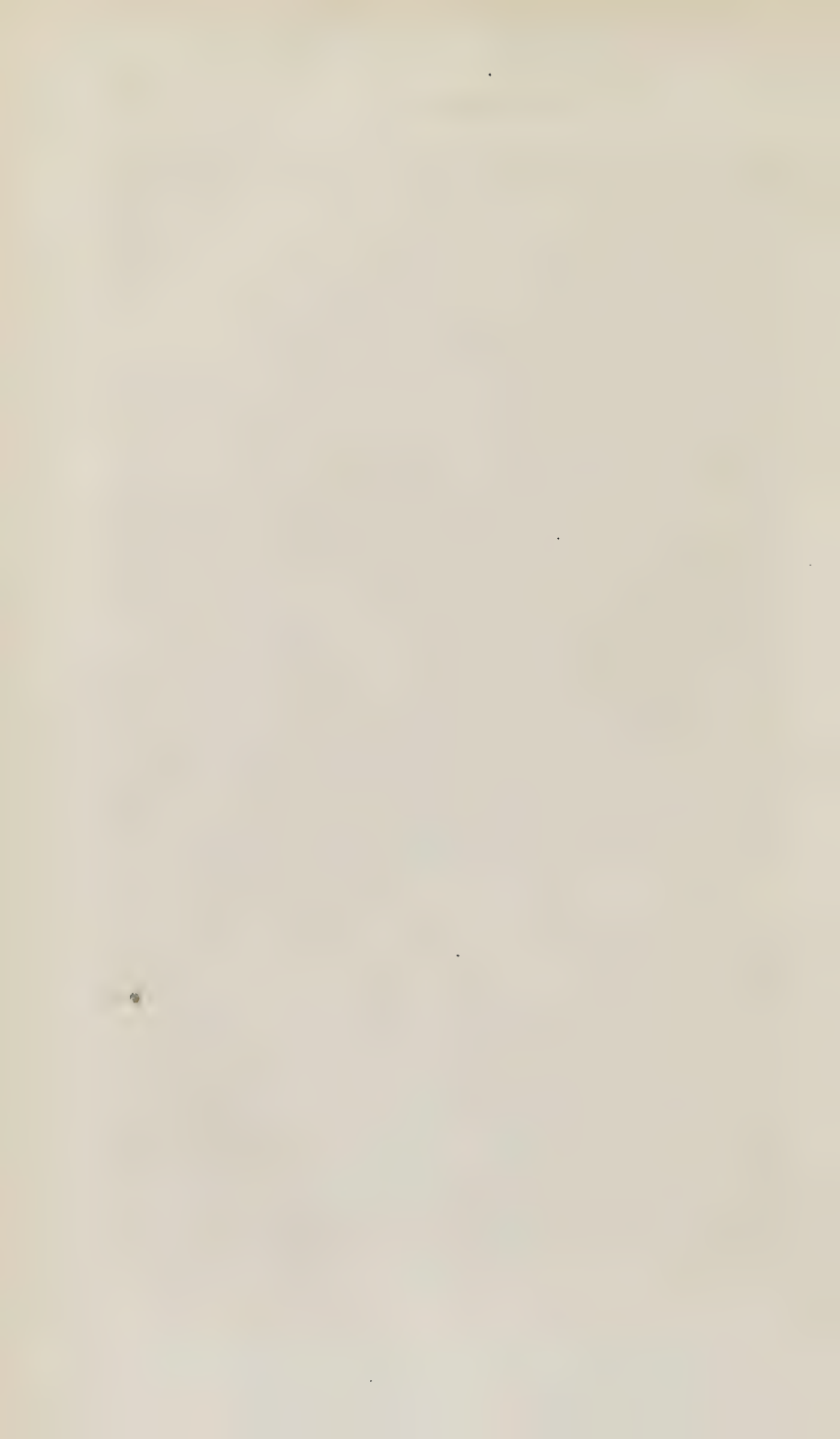
*Extract-Sediment.* If we extract fresh or dry vegetable substances with water, we obtain colorless solutions, which become dark-colored by evaporation in the air; if we treat the extract-like residue with water, there remains mostly a dark-colored body, which is called extract-sediment; this is soluble in alkalies, and agrees in its relations with the ulmin-substances and those of humin.

Extract-sediment.

To the general products of putrefaction and decay belong *brown coal* and *bituminous coal*.

Brown and bituminous coal.





# INDEX.

## A

ABSINTHIN, 429

Acetal, 164

Acetyl, acetate of oxychloride, 136

— bromide of, 141

— carbonate of oxychloride of, 135

— camphorate of oxychloride of, 182

— chloride of, 135

— formate of oxychloride of, 136

— hydrate of, 132

— oxyhydrate of, 130

— oxysulphide of, 182

— oxychloride of, 182

— oxysulphochloride of, 182

Acetyl-platinchloride-platinchloride, 136

Acetyl-urea, 325

Acetamid, 133

Acetonitryl, 136

Acetonyl, 145

— oxide of, 145

Aceton, 145

Acid, acetic, 132

— acephoric, 146

— acephosgenic, 146

— achilleic, 305

— aconitic, 287

— acrylic, 143

— adipinic, 180

— allanturic, 345

— alloetinic, 253

— alloeresinic, 254

— alloxanic, 341

— allitric, 345

— allophanic, 337

— alphaorsellic, 406

— amelinic, 343, 344

— amid-camphoric, 181

— ampelinic, 236

— amido-chrysamminic, 254

— amygdalinic, 428

— amyl-sulphohydric, 114

— amyloxyd-sulphocarbonic, 114

— amyloxyd-oxalic, 284

— amyloxyd tartaric, 292

— anacardic, 277

— anabenic, 344

— anemoninic, 267

— anemonic, 267

— angelic, 173

— anilic, 359

— anilocyanic, 361

Acid, anisylous, 216

— anisyllic, 216

— anthranilic, 211, 413

— antitartaric, 293

— apocrenic, 459, 461

— apophyllenic, 376

— asparagic, 259

— azulmic, 311

— azomarcic, 271

— bebeeruic, 305

— behenic, 157

— behylic, 157

— behynylic, 162

— benzaminic, 247

— benzilic, 225

— benziminic, 228

— benzinic, 228

— benzoic, 243

— betaorsellic, 406

— bibromsalicylous, 209

— bibromsalicylic, 213

— bichlorsalicylous, 209

— bichlorsalicylic, 213

— bichloracetie, 136

— bichlorbutyric, 150

— bichlorphenolic, 201

— bichloranisyllic, 217

— bichlorbenzoic, 246

— bichlor-valerianic, 152

— bilifulvinic, 458

— binitro-salicylic, 213

— —benzoic, 244, 246

— —anisyllic, 218

— —cinnamic, 249

— —cuminic, 252

— bisulphonaphthalin-sulphuric, 242

— bohea-tannic, 400

— bog-butyric, 158

— boletic, 305

— brom-phenolic, 201

— —phenissic, 201

— —anisyllic, 218

— —benzoic, 246

— brunolic, 201

— butyric, 148

— caffeeic, 401

— cainca, 427

— campholic, 262

— camphoric, 181

— —hydrate, 182

— camphoranimic, 182

- Acid, camphorammic, 181  
 — camphoranilic, 359  
 — capric, 155  
 — caprinic, 156  
 — capronic, 153  
 — caprylic, 155  
 — carbanilic, 359  
 — carbobenzoic, 249  
 — caryophyllic, 210  
 — carminic, 421  
 — catechuic, 400  
 — catechu-tannic, 397, 395  
 — cerebrie, 280  
 — cerotinic, 116  
 — cerosinic-cerossylic, 116  
 — ceric, 167  
 — cerossic, 162  
 — cerotic, 162  
 — cethyloxyl-sulphocarbonic, 115  
 — — — — — sulphuric, 115  
 — cetraric, 410  
 — chinonic, 194  
 — chinovic, 431  
 — chelidonic, 300  
 — chiococcic, 427  
 — chlorphenessic, 201  
 — chlorphenissic, 201  
 — chlorphenussic, 202  
 — chloranisylic, 218  
 — chloroniceinic, 192  
 — chlorsalicylic, 201  
 — chloroxal-tartaric, 284  
 — chlor-succylic, 144  
 — chloranilic, 197  
 — chloranilamidic, 198  
 — chlorbenzoic, 246  
 — chlormellissic, 116  
 — chlorsuccinic, 144  
 — chlorformyl-sulphochloride-sulphuric,  
   123  
 — — — — — chlorelayl-hyposulphuric, 124  
 — chloracetic, 138  
 — chlorcerotinic, 116  
 — chlorformic, 122  
 — cholic, 350, 351  
 — choleinic, 350, 352  
 — choloidic, 279  
 — cholalic, 278  
 — cholesteric, 280  
 — chrysamminic, 253  
 — chrysophanic, 410  
 — chrysanic, 210  
 — chrysanic, 413  
 — cinnamic, 248  
 — citric, 297  
 — citraconic, 295  
 — — — — — hydrous, 295  
 — — — — — anhydrous, 295  
 — — — — — copaivic, 271  
 — cocinic, 156  
 — cocylic, 156  
 — cokinic, 423  
 — coumarylous, 214  
 — coumarylic, 214  
 — copper-fulminic, 330  
 — crenic, 459, 461  
 — croconic, 308  
 Acid, cuminic, 251  
 — — — — — cuminylic, 251  
 — — — — — cyanic, 323  
 — — — — — hydrate of, 324  
 — — — — — cyanurenic, 336  
 — — — — — cyanuric, 336  
 — — — — — cyanylic, 332  
 — — — — — dammaric, 271  
 — — — — — decachlorbassiac, 162  
 — — — — — diluturic, 345  
 — — — — — doeglinic, 175  
 — — — — — elayl-sulphuric, 127  
 — — — — — elayl-hydrosulphuric, 127  
 — — — — — elaidic, 174  
 — — — — — ellagic, 403  
 — — — — — erucaic, 176  
 — — — — — erythric, 340, 406  
 — — — — — erythroleinic, 409  
 — — — — — ethalic, 158  
 — — — — — ether-carbonic, 107  
 — — — — — etheroxyd-chlorcarbonic, 107  
 — — — — — ether-sulphocarbonic, 107  
 — — — — — ether-sulphuric, 108  
 — — — — — ether-sulphophosphoric, 106  
 — — — — — ether-phosphoric, 105  
 — — — — — ether-myristic, 165  
 — — — — — ether-sulphacetic, 165  
 — — — — — ether-stearic, 166  
 — — — — — ether-tartaric, 292  
 — — — — — ether-camphoric, 185  
 — — — — — ether-oxalic, 283  
 — — — — — ethionic, 128  
 — — — — — ethyl-bioxyd-sulphocarbonic, 104  
 — — — — — ethyl-selenhydric, 110  
 — — — — — ethyl-hydrosulphuric, 110  
 — — — — — euphorbic, 306  
 — — — — — euchronic, 307  
 — — — — — everninic, 408  
 — — — — — evernic, 406  
 — — — — — fellinic, 279  
 — — — — — flavin-sulphuric, 414  
 — — — — — formic, 119  
 — — — — — formyl-sulphochloride-sulphuric, 122  
 — — — — — fumaric, 286  
 — — — — — fungic, 305  
 — — — — — gallerythric, 402  
 — — — — — gallic, 402  
 — — — — — gaultheric, 218  
 — — — — — geic, 459, 460  
 — — — — — gluten-hyposulphuric, 243  
 — — — — — glycerin-phosphoric, 434  
 — — — — — glycocoll-nitric, 348  
 — — — — — glycocoll-sulphuric, 348  
 — — — — — gnidic, 306  
 — — — — — guaiac, 220  
 — — — — — gyrophanic, 406  
 — — — — — hemipinic, 304  
 — — — — — hematin-nitric, 203  
 — — — — — hidantoinic, 346  
 — — — — — hippuric, 249  
 — — — — — humopinic, 375  
 — — — — — humintannic, 400  
 — — — — — humic, 459  
 — — — — — hydrocyanic, 312  
 — — — — — hydroferrocyanic, 317  
 — — — — — hydroferriecyanic, 319  
 — — — — — hydromargaric, 161

- Acid, hydromargaritic, 161  
 — hydromargaritin-sulphuric, 161  
 — hydro-oleic, 175  
 — hydrotri-sulphurenic, 334, 335  
 — hydrothiocyanic, 336  
 — hydro-sulphurenic, 334, 335  
 — hydro-sulphbiurenic, 334, 335  
 — hydro-bisulphurenic, 335  
 — — tri-sulphurenic, 335  
 — hydrosulpho-mellanic, 332  
 — hydrochrom-cyanic, 322  
 — hydroplatin-cyanic, 322  
 — hydrosilver-cyanic, 322  
 — hydrosulpho-cyanic, 324, 325  
 — hydrobisulpho-cyanic, 324, 328  
 — hydrorhodanic, 325  
 — hydroxanthanic, 325  
 — hydrohyper-sulphocyanic, 328  
 — hydroxanthic, 328  
 — hydrosulphomellanic, 333  
 — hydurilic, 345  
 — hyperuric, 346  
 — hyocholic, 352  
 — hyposulph-indigotic, 413  
 — igastric, 306  
 — inosinic, 350  
 — indigo-blue-sulphuric, 413  
 — isamic, 415  
 — isatinic, 415  
 — isatin-sulphuric, 414  
 — isæthionic, 127  
 — itaconic, 294  
 — japonic, 404  
 — kaffeeic, 397  
 — kakodylic, 387  
 — kinic, 303  
 — krameric, 305  
 — komenic, 302  
 — lactic, 143  
 — lantanuric, 340  
 — laurostearic, 157  
 — lecanoric, 407  
 — lecanoparic, 407  
 — lecanotatic, 406  
 — leucoturic, 345  
 — lichen-stearic, 277  
 — lichen, 404  
 — lipinic, 179  
 — — hydrate of, 79  
 — lithic, 338  
 — lithofellinic, 278  
 — lizarinic, 418  
 — madiac, 158  
 — malic, 287  
 — malaminic, 289  
 — margaric, 159  
 — margarin-sulphuric, 161  
 — meconic, 301  
 — mellitic, 306  
 — mellanurenic, 337  
 — melaminic, 289  
 — mellissic, 163  
 — melan-gallic, 404  
 — mercury-fulminic, 330  
 — mesoxalic, 306  
 — mesityloxyd-sulphuric, 146  
 — mesito-sulphuric, 238  
 Acid, metatartaric, 292  
 — metacetic, 147  
 — metamargaric, 161  
 — meta-oleic, 175  
 — metapectic, 446  
 — meta-mucic, 299  
 — methyloxyd-carbonic, 98  
 — methyloxyd-chlorcarbonic, 98  
 — methyloxyd-tartaric, 292  
 — methyloxyd-sulphocarbonic, 99  
 — methyloxyd-sulphuric, 99  
 — methyl-hydrosulphuric, 99  
 — morinic, 401  
 — morin-tannic, 397  
 — moringaic, 173  
 — mucic, 299  
 — myristic, 157  
 — mykomelinic, 345  
 — myronic, 428  
 — myroxyllic, 249  
 — narcotinic, 376  
 — naphthyl-sulpho-sulphuric, 249  
 — nitro-synapyllic, 327  
 — nitro-toluylic, 251  
 — — benzoic, 247  
 — — ferricyanhydric, 321  
 — — purreeic, 423  
 — — valerianic, 151  
 — — phthalinic, 183  
 — — chloroniceinic, 193  
 — — chlorphenollic, 201  
 — — phenollic, 201  
 — — phenessic, 201  
 — — salicylic, 214, 413  
 — — salicylous, 210  
 — — coumarylous, 215  
 — — lithofellinic, 278  
 — — anisylic, 218  
 — — chloroniceinic, 193  
 — — purreeic, 423  
 — oenanthic, 154  
 — oleic, 174  
 — oleinic, 174  
 — olinic, 174  
 — olidic, 158  
 — opianic, 304, 375  
 — opian-sulphurous, 304  
 — orsellinic, 407  
 — orceic, 408  
 — oxalic, 281  
 — oxamid-oxalic, 283  
 — oxaminic, 283  
 — oxanilic, 359  
 — oxychlor-kakodylic, 388  
 — oxyfluor-kakodylic, 389  
 — oxaluric, 344  
 — oxypikrinnitric, 423  
 — oxychlorokakodylic, 388  
 — oxyfluorokakodylic, 389  
 — oxypikrin-nitric, 204  
 — palmitic, 157, 175  
 — parabanic, 330, 344  
 — parafumaric, 286  
 — parællagic, 403  
 — parapectic, 446  
 — paracholic, 351  
 — paracyanic, 312



- Acid, paramidic, 307  
 — paratartaric, 293  
 — pectic, 446  
 — pectosic, 446  
 — pelargonic, 153  
 — penta-chlorphenolic, 201  
 — phthalamic, 183  
 — phthalinic, 182  
 — phthalinilic, 359  
 — ——— hydrate of, 183  
 — phenol-sulphuric, 199  
 — phosphorinic, 105  
 — phosphacetic, 146  
 — phtalinic, 182  
 — phtalamic, 183  
 — phtalic, 182  
 — phtalanilic, 359  
 — pieramyloxyd-formic, 228  
 — pieramyloxyd-sulphuric, 228  
 — pikranisic, 205  
 — pikrinic, 201  
 — pikrin-nitric, 202  
 — pimelinic, 180  
 — pimaric, 271  
 — pinic, 271  
 — pimentic, 220  
 — polygalic, 432  
 — propionic, 147  
 — purpuric, 343  
 — purpurin-sulphuric, 414  
 — purpur-sulphuric, 413  
 — pyromucic, 302  
 — pyromuconic, 303  
 — pyro-olivinic, 428  
 — pyroracemic, 296  
 — pyrotartaric, 296  
 — pyroterebinic, 184  
 — pyropectic, 446  
 — pyrouic, 336  
 — pyromorinic, 400  
 — pyrogallic, 404  
 — pyromorin-tannic, 402  
 — pyro-tannic, 403  
 — pyro-olivinic, 428  
 — quadrichlor-butyrlic, 150  
 — ——— -valerianic, 152  
 — quercitronic, 402  
 — racemic, 293  
 — rhodizonic, 308  
 — rhabarberic, 410  
 — ricinic, 175  
 — roccellous, 407  
 — roccifucic, 406  
 — roccellic, 406  
 — roccie, 406  
 — rosaic, 346  
 — rosolic, 201  
 — rufo-morinic, 401  
 — rufingallic, 403  
 — redgallic, 403  
 — rubigallic, 403  
 — rubinic, 404  
 — rubrin-nitric, 203  
 — rutilin-sulphuric, 427  
 — saccharic, 298  
 — salicylous, 207  
 — salisyllic, 210  
 Acid, salicyl-amidic, 211  
 — santonic, 432  
 — santalic, 422  
 — sebacic, 180, 181  
 — silver-fulminic, 330  
 — silvic, 270  
 — solanic, 306  
 — stearic, 160  
 — stearophanic, 162  
 — succinic, 177  
 — ——— hydrate of, 177  
 — succin-sulphuric, 179  
 — suberic, hydrate of, 180  
 — suberanilic, 359  
 — sulpho-camphoric, 182  
 — sulph-anise-sulphuric, 206  
 — sulpho-naphtalid-sulphuric, 233  
 — sulpho-tolid-sulphuric, 237  
 — ——— -cymid-sulphuric, 237  
 — ——— -cumid-sulphuric, 237  
 — ——— -benzo-sulphuric, 254  
 — ——— -benzid-sulphuric, 223  
 — ——— -cinn-sulphuric, 249  
 — sulphomethyl-sulphuric, 98, 123  
 — sulphokakodyl-sulphuric, 387  
 — sulphethyl-sulphuric, 110  
 — sulphamyl-sulphuric, 113  
 — sulphelalyl-sulphuric, 126  
 — sulphanilic, 360  
 — sulphopurpuric, 413  
 — sulphacetic, 142  
 — sulphacetyl-sulphuric, 142  
 — sulphethyl-sulphuric, 106  
 — sulpho-cymid-sulphuric, 239  
 — sulphophenetol-sulphuric, 206  
 — sulphopianic, 305  
 — tannic, 395, 398  
 — tanno-melanlic, 403  
 — tannoxylic, 402  
 — tartaric, 289  
 — tartralic, 292  
 — tartrelic, 293  
 — terecric, 173  
 — terephthalic, 184  
 — tetrachlor-benzoic, 244, 246  
 — trichlor-benzoic, 246  
 — terebinic, 184  
 — terebenzinic, 193  
 — terchlorphenolic, 201  
 — thiomelanlic, 109  
 — toluyllic, 239, 251  
 — trygenic, 338  
 — trinitrosalicylic, 214  
 — tribromsalicylic, 213  
 — thionuric, 342  
 — tobacic, 306  
 — ulmic, 459, 460  
 — uric, 338  
 — uramilic, 342  
 — urenoxydamid-oxalic, 338  
 — usnic, 408  
 — viridin-sulphuric, 414  
 — veratric, 304  
 — valerianic, 151  
 — viridinic, 401  
 — xanthopenic, 305  
 — xanthoproteinic, 450

- Acid, zinc-fulminic, 330  
 Aconitin, 374  
 Acrolein, 142, 186  
 Acrolein-ammonia, 142  
 Acryl, 142  
 Acryl, oxyhydrate of, 142  
 Aesculin, 430  
 Alanin, 131, 346, 348  
 Albumen, 448, 452  
 ——— vegetable, 452  
 Alcohol, 102  
 Aldehyd, 117, 130  
 Aldehyd-ammonia, 131  
 Aldehyd-resin, 131  
 Alizarin, 418  
 Alkanna-red, 420  
 Alkanna-green, 420  
 Alkalids, 346  
 Alkaloids, 354  
 Allyl-group, 168  
 Allyl, 168  
 ——— sulphocyanide of, 327  
 ——— oxide of, 169  
 Allantoin, 339  
 Alloxan, 340  
 Alloxantin, 339, 341, 344  
 Alloxantoin, 339  
 Aloin, 430  
 Alphaorcein, 409  
 Althæin, 289  
 Alumina, tartrate of, 291  
 ——— acetate of, 134  
 Almond, bitter, oil, 225  
 Amarin, 365  
 Amasatin, 415  
 Amasetin, 415  
 Amarin, 225  
 Amber oil, 264  
 Amber, 273  
 Amber-bitumen, 274  
 Ambrain, 280  
 Amisatin, 415  
 Ammeln, 368  
 Ammelid, 368  
 Anisol, 205  
 Ammonia, gum, 275  
 ——— malates of, 288  
 ——— camphorate of, 181  
 ——— chlorsuccinate of, 145, 179  
 ——— succinate of, 178  
 ——— salicylate of, 208  
 ——— acetate of, 133  
 ——— formate of, 120  
 ——— anisylate of, 217  
 ——— benzoate of, 244  
 ——— binitrosalicylate of, 213  
 ——— chelidonate of, 300  
 ——— chinate of, 303  
 ——— kinnate of, 303  
 ——— chloranibamidate of, 198  
 ——— chloranilate of, 197  
 ——— chlorcarbathaminatate of, 141  
 ——— chloracetate of, 139  
 ——— chlorniceinate of, 193  
 ——— chrysanisate of, 210  
 ——— cyanate of, 324  
 ——— fumarate of, 286  
 Ammonia, oxalates of, 282  
 ——— copperfulminate of, 331  
 ——— leucoturate of, 345  
 ——— lipinate of, 180  
 ——— malaminatate of, 289  
 ——— margarinate of, 159  
 ——— mellithate of, 306  
 ——— nitrobenzoate of, 247  
 ——— nitrophthalinate of, 183  
 ——— phthalinate of, 183  
 ——— propionate of, 147  
 ——— rubianate of, 203  
 ——— salicylate of, 211  
 ——— salicylite of, 208  
 ——— valerianate of, 151  
 ——— tartrate of, 290  
 ——— simple tartrate of, 290  
 ——— purpurate of, 290  
 Ammonium, cyanide of, 315  
 ——— sulpho-cyanide of, 326  
 ——— ferro-cyanide, 317  
 Amyl-formyl, 124  
 Amyl-amin, 357  
 Amyl-urea, 325, 367  
 Amyl, 112  
 Amyl-capronyl, oxide of, 153  
 Amyl-mercaptan, 114  
 Amyl, acetate of, 166  
 ——— sulphocyanide of, 327  
 ——— valerianate of, 327  
 ——— oxalate of, 283  
 ——— oxyhydrate of, 113  
 ——— borate of, 113  
 ——— silicate of, 113  
 ——— nitrate of, 113  
 ——— nitrite of, 113  
 ——— protosulphide of, 114  
 ——— bi-sulphide of, 114  
 ——— iodide of, 114  
 ——— bromide of, 114  
 ——— chloride of, 114  
 ——— oxide of, 112  
 ——— sulpho-carbonate of, 114  
 ——— oxamate of, 283  
 ——— spirits of, 283  
 Amygdalin, 428  
 Amylum, 439  
 Amylen, 128  
 ——— borate of, 113  
 ——— bisulphide of, 114  
 ——— bromide of, 114  
 ——— chloride of, 114  
 ——— iodide of, 114  
 ——— oxide of, 112  
 ——— oxyhydrate of, 113  
 ——— protosulphide of, 114  
 ——— nitrite of, 113  
 ——— nitrate of, 113  
 ——— silicate of, 113  
 Anacardium oil, 278  
 Anchusin, 420  
 Anchusa-green, 420  
 Anemonin, 267  
 Angelicyl, 173  
 Anilin, 223, 358  
 ——— cyanide of, 360  
 Anilin-urea, 367

- Anilids, 359  
 Anise oil, 205  
 ——— camphor, 206  
 Anisoin, 206  
 Anisyl, 216  
 ——— imid-amid, 216  
 ——— bioxychloride of, 217  
 ——— bioxybromide of, 217  
 ——— nitrid, 217  
 Anime resin, 272  
 Anthiarin, 430  
 Anthracid, 233  
 Anthracin, 233  
 Antimony bases, 390  
 ——— basic tartrate of, 291  
 Antimony-potassa, basic tartrate of, 291  
 Appiin, 430  
 Apposepidin, 347  
 Arabin, 442  
 Archil, 408  
 Aricin, 383  
 Arsenic bases, 386  
 Arsenethyl, 389  
 Arsenic-ethyl, amin-oxide of, 389  
 ——— 389  
 Asarum camphor, 267  
 Asarit, 267  
 Asarin, 267  
 Asafetida, 275  
 Asparagin, 259  
 Asphalt, 274  
 Assamar, 201  
 Athamantin, 429  
 Athamanta-oreoselinum, oil of, 264  
 Atropin, 373  
 Azocarbyls, 310  
 Azolitmin, 409  
 Azoerythrin, 409  
 Azobenzil, 225  
 Azobenzoilid, 225  
 Azobenzoyl, azobenzoid, azobenzoidin, 225  
 Azo-oxybenzid, 222  
 Azobenzid, 222
- B
- Baryta, acetate of, 334  
 ——— cyanurate of, 337  
 ——— allophanate of, 337  
 ——— acrate of, 143  
 ——— malate of, 288  
 ——— alphaorsellate of, 406  
 ——— formate of, 120  
 ——— amyloxyd-sulphate of, 114  
 ——— benzoate of, 244  
 ——— caprinate of, 156  
 ——— caprate of, 155  
 ——— kinnate of, 303  
 ——— chlorniceinate of, 193  
 ——— chlorphenissate of, 202  
 ——— citroconate of, 295  
 ——— citrate of, 298  
 ——— croconate of, 308  
 ——— cyanate of, 337  
 ——— cyanurate of, 337  
 ——— inosinate of, 350  
 ——— itaconate of, 295  
 ——— lipinate of, 180
- Baryta, margarinate of, 159  
 ——— mellitate of, 306  
 ——— mesityloxyd-sulphate of, 146  
 ——— methyloxyd tartrate of, 292  
 ——— nitrotoluylate of, 251  
 ——— pelargonate of, 155  
 ——— purpurate of, 343  
 ——— salicylite of, 208  
 ——— sulphamyl-sulphate of, 113  
 ——— valerianate of, 151  
 ——— zincfulminate of, 331  
 ——— urate of, 340  
 Barium, zinc-cyanide of, 322  
 ——— ferro-cyanide of, 318  
 ——— ferri-cyanide of, 319  
 ——— mercury-cyanide of, 322  
 ——— cyanide of, 316  
 Bases, organic, 354  
 Bdelium, 275  
 Bebeerin, 384  
 Behynyl, 162  
 Behyl, 157  
 Benzanil, 225  
 Benzanilid, 359  
 Benzoin, 224  
 ——— -resin, 274  
 Benzoinamid, 274  
 Benzoinam, 274  
 Benzin, 221  
 Benzid, 221  
 ——— chloride of, 222  
 Benzidin, 358  
 Benzidam, 358  
 Benzoen, 236  
 Benzolin, 365  
 Benzol, 221  
 Benzil, 225  
 Benzil-imid, 225  
 Benzilam, 225  
 Benzhydramid, 225, 227  
 Benzoyl, 243  
 ——— sulpho-cyanide of, 226  
 ——— oxide of, 243  
 ——— bioxysulphide of, 245  
 ——— chloride of, 245  
 ——— bioxychloride of, 245  
 ——— bioxybromide of, 245  
 ——— bioxyiodide of, 245  
 ——— acetyl-chlorate of bioxychloride  
 of, 245  
 ——— nitrid, 246  
 Benzolin, 365  
 Benzoylazotid, 225  
 Benzolon (Benzostilbin), 227  
 Benzoates, 244  
 Benzo-nitryl, 246  
 Benzon, 250  
 Benzyl, 240  
 ——— chloride of, 240  
 ——— hydrochlorate of chloride of, 241  
 ——— nitrid, 241  
 Berberin, 383  
 Berry-red, 418  
 Berzelius and Mercet's combination, 123  
 Bergamot-oil, 263  
 Betula resin, 272  
 Betulin, 272

- Betarocēin, 410  
 Betaorcin, 410  
 Betaroccin, 482  
 Betaquinin, 282  
 Bibenzamid, 244  
 Bibromisatin, 415  
 Bibromsalicylimid-amid, 210  
 Bibromanilin, 362  
 Bicamphorimid, 181  
 Bichlorchinon, 196  
 ————— colorless, 196  
 ————— yellow, 196  
 ————— violet, 196  
 Bichlornaphthalid, 241  
 Bichlorbenzoyl, hydrochlorate of chloride of, 246  
 Bichlorbenzoyl, hydrochlorate of super-chloride of, 246  
 Bichloracetyl, 137  
 ————— chloride of, 135  
 ————— acetate of oxychloride, 137  
 ————— formate of, 137  
 Bichlorbutyryl, 150  
 ————— oxyhydrate, 150  
 Bichlorbutyral, 150  
 Bichlorsalicylimidamid, 209  
 Bichlorvaleryl, 152  
 Bichloroanthyl, 154  
 Bichlorisatin, 415  
 ————— oxyhydrate of, 155  
 Bichloranilin, 362  
 Bicyanomelanilin, 361  
 Biethyl-amylamin, 367  
 Bilifulvin, 458  
 Bimethylamin, 354  
 Binitro-melanilin, 367  
 Binitro-anisol, 212  
 ——— -anisidin, 212  
 Binitro-benzid, 222, 241  
 Binitro-azobenzid, 223  
 ——— -anthracid, 234  
 ——— -tolid, 236  
 ——— -lid, 237  
 ——— -cumid, 237  
 ——— -mesitol, 238  
 ——— -mesidin, 238  
 ——— -naphthalid, 242  
 Bioxyprotein, 453  
 Birch oil, 264  
 Biphosmethyl, 385  
 Bisuccinamid, 178  
 Bismæthyl (Bismuth-ethyl), 393  
 Bitter-principles, 425  
 Blue, Berlin, 30  
 ——— Turnbull's, 30  
 ——— basic, 30  
 Bohea tanning, 400  
 Brazilin, 420  
 Brucia, 380  
 Brucin, 380  
 Bromacetyl, 141  
 ————— oxyhydrate of, 141  
 Bromal, 141  
 Bromoform, 121  
 Bromanilin, 362  
 Bromcinchonin, 381  
 Bromphenetol, 206  
 Bromtereben, 260  
 Bromterpentin, 260  
 Bromanise-oil, 205, 207  
 Bromcinnamin, 231  
 Bromthionessal, 226  
 Brombenzid, 241  
 Buckthorn berries, 424  
 Butyryn, 186  
 Butyral, 148  
 Butyr-amid, 149  
 Butyryl, 148  
 ————— oxyhydrate, 148  
 ————— protochloride, 149  
 Butyron, 150  
 Butyromitryl, 149  
 Butyrates, 149  
 Butylamin, 357  
 Butyren, 128  
 ————— gas, 111, 128
- C
- Cadmium, cyanide of, 316  
 Caffein, 369  
 ————— hydrochlorate of, 369  
 ————— sulphate of, 369  
 ————— nitrate of, 369  
 Caïncin, 427  
 Cajeput oil, 261  
 Calcium, mercury-cyanide of, 322  
 Camphene, 256  
 Camphilen, 259  
 Camphin, 262  
 Camphor, formation of, 257  
 ————— helenium, 266  
 ————— oil, 261  
 ————— Borneo, 261  
 ————— anemone, 267  
 ————— asarum, 267  
 ————— cedar, 265  
 ————— cantharides, 267  
 ————— tobacco, 267  
 ————— pulsatillen, 267  
 ————— laurus, 261  
 ————— marjorana, 266  
 ————— monarda, 266  
 ————— menthen, 265  
 ————— violet, 266  
 ————— sassaparilla, 266  
 Camphron, 262  
 Camphoranilid, 359  
 Cane-sugar, 443  
 Cantharides camphor, 267  
 Canthariden, 267  
 Caoutchin, 264  
 Caoutchouc, 276  
 Capronyl, 153  
 Capron, 153  
 Capronates, 153  
 Caprinyl, 156  
 ————— oxyhydrate, 156  
 ————— oxychloride, 156  
 Caprylon, 155  
 Caramel, 439  
 Capsicin, 385  
 Caproyl, 114  
 Carvacrol, 200  
 Caruen, 263



- Carbohydrates, 434  
 Carbyls, 281  
     — sulphate of, 127  
 Carthamin, 420  
 Carmin, 421  
 Carnen, 263  
 Carbanilid, 359  
 Carbamid, 367  
 Carbothialdin, 132, 371  
 Carbon, sesquichloride of, 139  
 Casein, 454  
 Cascarilla oil, 264  
 Castorin, 280  
 Catechin, 400  
 Catechu tannin, 397  
 Cedar-oil, 265  
 Cedar-camphor, 265  
 Cedret, 201  
 Cellulose, 434  
 Cerotin, 116  
 Cernauba wax, 167  
 Cerotyl, 116, 162  
     — oxide of, 162  
     — cerotate of, 166  
     — oxyhydrate of, 166  
     — sulphate of, 166  
 Cerossyl, 115, 162  
 Cerosinyl, 166  
     — oxide of, 166  
 Cerosin, 166  
 Cerin, 116, 162  
 Ceroten, 129  
 Cerotin, 116  
 Cethyl, oxyhydrate of, 115  
     — chloride of, 115  
     — ethalate of, 115  
 Cetrarin, 410  
 Ceten, 129  
 Cheese, 454  
 Chelerythrin, 377  
 Chelidonin, 377  
 Chinarothe, 399  
 Chinoidin, 383  
 Chinidin, 382  
 Chinin, 382  
     — hydrochlorate of, 382  
     — sulphate of, 382  
 Chinotin, 382  
 Chinolin, 363  
 Chinon, 194  
 Chitin, 455  
 Chiococcin, 427  
 Chinon-amid, 455  
 Chinovin, 431  
 Chloral, 138  
 Chloralid, 138  
 Chloracetyl, 137  
     — chloride of, 138  
     — oxychloride of, 139  
     — formate of oxybichloride, 141  
     — acetate of oxybichloride, 141  
     — chlorformate of oxybichloride, 141  
     — bichloracetate of oxybichloride, 141  
     — chloracetate of oxybichloride, 141  
 Chloracetyl, chloroanthate of oxychloride, 155  
     — chlor-succinate of oxychloride, 179  
     — oxide of, 137  
     — oxyhydrate of, 137  
     — terchloride of, 139  
     — oxybichloride of, 140  
     — sulphochloride of, 140  
     — oxybromide, 140  
     — chlorbromide of, 140  
     — carbonate of oxychloride of, 140  
     — chlor-succinate of oxychloride of, 179  
     — oxalate of bichloride of, 284  
 Chlorformyl, 122  
     — chloride of, 122  
     — bichloride of, 122  
     — oxychloride of, 123  
     — sulphochloride of, 123  
     — bichloracetate of oxychloride, 137  
     — chlor-sulphide, 123  
     — acetate of oxychloride, 136  
     — chlorformate of oxychloride, 123  
     — sulphite, 123  
     — terchloride, 123  
 Chlorbenzin, 241  
 Chlor-camphen, 260  
 Chlor-tereben, 260  
 Chlor-turpentin, 260  
 Chlorbutyron, 149  
 Chloracrol, 154  
 Chlorallyl, 170  
 Chloranilin, 362  
 Chlorcyananilid, 360  
 Chlornicin, 357  
 Chlorophyl, 417  
 Chloramyl, 114  
 Chlorchinon, 195  
 Chlormesitol, 238  
 Chlormesityl, 146  
 Chloromethyl, 100  
 Chloroform, 121  
 Chloroxal-ether, 284  
 Chloroxethamid, 284  
 Chloroxamethan, 284  
 Chlorparacetyl, *vide* methylen-formyl, 126  
 Chlor-picramyl, 226  
 Chlor-stibeathyl, 393  
 Chlorotolid, 236  
 Chlorchinon, 196  
 Chloroxalamid, 284  
 Chloranil, 197  
 Chloranilam, 198  
 Chloranilammon, 198  
 Chloranil-amid, 197  
 Chlorhydroanil, 197  
 Chloronicin, 192  
 Chloronicein-amid, 193  
 Chloranise-oil, 207  
 Chlor-isatin, 415  
 Chlor-pikrin, 204  
 Chlor-saligenin, 216  
 Chlor-cinnamin, 231  
 Chloraldehyd, 139

- Chlor-ethyl, 111  
 Chloroacetamid, 140  
 Chlorcarbæthamid, 140  
 Chlor-succyl, 144  
 Chlorcuminy, 363  
 Chlorcinnapryl, 363  
 Chlorcaffein, 369  
 Chlorisatin, 369  
 Cholepyrrhin, 458  
 Cholestrophan, 343, 344  
 Cholesterin, 279  
 Cholesterilens, 280  
 Cholacrol, 279  
 Chondrin, 457, 454  
 Chromium, oxalate of, 283  
 ——— cyanide, 316  
 Chrysorhamnin, 424  
 Chrysaminamid, 254  
 Chrysen, 234  
 Chrysid, 234  
 Cinnanilid, 359  
 Cinchonin, 381  
 ——— sulphate of, 381  
 ——— hydrochlorate of, 382  
 Cinchona, 381, 399  
 Cinchonetin, 381  
 Cinnyl, cimmyl, 248  
 ——— bioxychloride, 249  
 Cinnamid, 230  
 Cinnamyl, 228  
 ——— oxide of, 228  
 ——— oxychloride of, 228  
 ——— nitrate of, 229  
 ——— sulphide of, 229  
 Cinnamon oil, 229  
 Cinnamein, 229  
 Cinnamin, 230  
 Cinnanilid, 359  
 Cisampeline, 383  
 Citrates, 297  
 Citraconates, 295  
 Citren, 263  
 Citrilen, 263  
 Clove oil, 264  
 ——— camphor, 264  
 Cobalt, cyanide of, 316  
 ——— sesquicyanide of, 316  
 Cocculin, 431  
 Cocinon, 156  
 Cocyl, 156  
 Codein, 374  
 Codeia, 374  
 Coffee-tannin, 397  
 Colophen, 260  
 Colchicin, 378  
 Columbin, 431  
 Coloring matters, 415  
 Collodium, 439  
 Colophon, 270  
 Copaiva, balsam, 271  
 ——— oil, 263  
 Copper, dicyanide, 316  
 ——— protocyaniide, 316  
 ——— acetate of, 134  
 ——— camphorate of, 182  
 ——— croconate of, 303  
 Copper, copper-fulminate of, 331  
 ——— ether-camphorate of, 185  
 ——— inosinate of, 350  
 ——— lactate of, 14  
 ——— oenanthate of, 154  
 ——— salicylite of, 209  
 Copal, 273  
 Corydalin, 381  
 Cork substance, 439  
 Coal, brown, 461  
 ——— bituminous, 461  
 Coniin, 363  
 Cotarnin, 376  
 Cotarnia, 376  
 Coumaryl, 214  
 Coumarin, 214  
 Cow-tree resin, 275  
 Creatin, 349  
 Creatinin, 370  
 ——— sulphate of, 370  
 Creosote, 199  
 Crystallin, 454  
 Crystalli tartari, 291  
 Cubeba oil and cubeba camphor, 264  
 Cucurmin, 422  
 Cudbear, 408  
 Cuminanilid, 359  
 Cumid, 237  
 Cumidin, 363  
 Cumin (Cumyl), 222, 237  
 Cumen, 239  
 Cuminol, 238  
 Cumyl, 238  
 ——— oxide of, 238  
 ——— chloride of, 238  
 ——— sulphide of, 238  
 ——— bioxysulphide of, 238  
 ——— bioxybromide of, 238  
 Cuminy, 251  
 ——— bioxychloride of, 252  
 ——— bioxybromide of, 252  
 Curarin, 380  
 Curcumin, 422  
 Cyanurates, 336-337  
 Cyanogen, sulphide of, 336  
 ——— protochloride of, 328  
 ——— metachloride of, 329  
 ——— bichloride of, 329  
 ——— protobromide of, 329  
 ——— protoiodide of, 329  
 ——— sulphide of, 336  
 ——— bromide of, 329  
 Cyano-oil, 268  
 Cyanogen, 328, 310  
 Cyanides, 313, 317  
 Cyanethyl, 147  
 Cyanamethyl, 136  
 Cyanamyl, 153  
 Cyanilin, 360  
 Cyancumidin, 363  
 Cyanethin, 365  
 Cymidin, 363  
 Cymid, 237  
 Cymin, 222, 239  
 Cynodin, 289  
 Cystin, 349

## D

Dammara resin, 271  
 Dammaryl, 271  
 Daturin, 373  
 Delphinin, 378  
 Delphenin, 223  
 Dextrine, 441  
 Dextrine-sugar, 444  
 Diaethylamin, 457  
 Diastase, 441  
 Difluan, 345  
 Disacryl, 143  
 Doeglyl, 175  
 Dracyl, 236  
 Dragon's-blood, 275  
 Dyslysin, 279  
 Dulcose, 433  
 Dulcin, 433

## E

Elaen, 129  
 Elayl-platinum, 127  
 Elayl, 125  
 — bisulphide, 125  
 — tetra-sulphide, 125  
 — iodide, 126  
 — bromide, 126  
 — chloride, 126  
 — oxychloride, 127  
 — sulphate, 127  
 — ether-sulphate, 126  
 Eleadin, 187  
 Elemi oil, 263  
 — resin, 272  
 Emetin, 373  
 Emeta, 378  
 Emulsin, 451  
 Erucyl, 176  
 Erytrarsin, 390  
 Erythrophenyl, 418  
 Erythrorotin, 410  
 Erythrolitmin, 409  
 Erythrolein, 409  
 Erythromannit, 408  
 Erythroglucin, 408  
 Erythrine, 406  
 Erythrine-ether, 407  
 Essential-soap, 190  
 Ethal, 115  
 Ether, 104  
 —, acetic, 164  
 — oxamid, 104  
 Ethylamin, 357  
 Ethylamylamin, 357  
 Ethyl-urea, 367  
 Ethyl, 100  
 — anisylate of, 219  
 — aconate of, 287  
 — adipinate of, 185  
 — acetate of, 164  
 — acrate of, 165  
 — allophanate of, 324  
 — behenate of, 166  
 — benzoate of, 252  
 — binitro-benzoate of, 252  
 — butyrate of, 166  
 — bromide of, 111

Ethyl, bichlor-bromide of, 111  
 — borate of, 105  
 — biether-phosphate of, 105  
 — bisulphide of, 109  
 — capronate of, 166  
 — caprate of, 166  
 — cyanurenate of, 166  
 — cyanate of, 325  
 — cerotinate of, 166  
 — carbonate of, 104  
 — chlorniceinate of, 193  
 — chlorformate of, 164  
 — chloracetate of, 164  
 — camphorate of, 185  
 — chrysanisate of, 210  
 — cinnamate of, 252  
 — citrate of, 298  
 — cuminate of, 252  
 — doeglinatate of, 176  
 — elaidate of, 176  
 — evernate of, 408  
 — fluoride of, 111  
 — formate of, 164  
 — fumarate of, 286  
 — hyperchlorate of, 106  
 — hippurate of, 252  
 — itaconate of, 295  
 — laurostearate of, 165  
 — mellitate of, 307  
 — margarate of, 307  
 — mucate of, 298  
 — nitrate of, 165  
 — nitrite of, 165  
 — nitro-benzoate of, 252  
 — nitro-cinnamate of, 252  
 — nitro-toluylate of, 252  
 — oxamine of, 283  
 — opianate of, 305  
 — oxalate of, 283  
 — oxide of, 101  
 — oxyhydrate of, 102  
 — oxychlor-chloracetate of, 165  
 — oleate of, 176  
 — orsellinate of, 407  
 — oenanthate of, 165  
 — phtalinate of, 185  
 — phosphate of, 105  
 — phosphite of, 105  
 — phosphide of, 385  
 — propionate of, 166  
 — protosulphide of, 109  
 — propionate of, 165  
 — pyro-mucate of, 302  
 — quadrichlor-butyrate of, 302  
 — sulphite of, 165  
 — sulphate of, 165  
 — sulpho-cyanide of, 327  
 — sulpho-carbonate of bioxide of, 107  
 — stearophanate of, 166  
 — sulpho-carbonate of, 165  
 — sebacylate of, 185  
 — succinate of, 184  
 — suberate of, 185  
 — salicylate of, 219  
 — terebenzinate of, 193  
 — tribasic phosphate of, 105  
 — tersulphide of, 109

Ethyl, toluylate of, 252  
 —, tartrate of, 292  
 — valerianate of, 165  
 — veratrate of, 304  
 Ethyl-formyl, 128  
 Euchron, 307  
 Eugenin, 220  
 Eupion, 129, 235  
 Euphorbium, 272  
 Euphorbia-resin, 272  
 Euxanthin, 422  
 Euxanthon, 423  
 Extract-sediment, 458

## F

Ferment oils, 268  
 Ferrocyanides, 318  
 Ferricyanides, 319  
 Ferrulyl, 171  
 Fibrin, 448, 452  
 Fibrin-protein, 153  
 Fibro-fibrin, 448  
 Fibroin, 454  
 Fichtelite, 236  
 Formal, 163  
 Formic oil, artificial, 193  
 Formyl, 117, 119  
 — acetate of oxychloride of, 136  
 — bromide of, 121  
 — bromiodide of, 122  
 — bichloride of, 121  
 — bichloracetate of oxychloride of, 137  
 — iodochloride of, 122  
 — formate of oxychloride of, 122  
 — iodide of, 120  
 — chloride of, 121  
 — sulphide, 120  
 — terchloride, 121  
 — oxychloride, 121  
 — sulphochloride, 122  
 Formanilid, 359  
 Fruit-sugar, 443  
 Fulminan, 330  
 Fulminates, 330, 331  
 Fumaramid, 286  
 Furfurin, 366, 194  
 Furfurol, 193  
 Fuselole, potato, 113

## G

Galbanum, 275  
 Galanga oil, 264  
 Gall brown, 458  
 Gall-nut tannin, 398  
 Gall-yellow, 398  
 Gallipot, 271  
 Gamboge, 275  
 Garancin, 420  
 Gaultherilen, 264  
 Gelatin sugar, 347  
 Gentianin, 423  
 Glaucin, 377  
 Glauco-picrin, 377  
 Globulin, 457  
 Gluten, vegetable, 442, 451  
 Glue, 456  
 —, bone, 456

Glue, cartilage, 457  
 Gyzcyrrhizin, 433  
 Glycyrrin, 433  
 Glycerin, 186, 433  
 Glycocoll, 346, 347  
 — hydrochlorate of, 347  
 — nitrate of, 347  
 — sulphate of, 347  
 — potassa, 347  
 — sulphate of potassa, 347  
 — nitrate of potassa, 348  
 — leadoxyd, 347  
 — copperoxyd, 347

Glycyl, oxide of, 186  
 — butyrate of, 186  
 — eleadinate of, 186  
 — laurostearinate of, 186  
 — myristicinate of, 186  
 — margarinate of, 186  
 — oleinate of, 186  
 — palmitinate of, 186  
 — stearophanate of, 186  
 — stearinate of, 186  
 — valerianate of, 186  
 Gold, protocyanide of, 317  
 — terycyanide of, 317

Grubengas, 95  
 Guaiacen, 220  
 Guaiac resin, 274  
 Guaiacol, 200  
 Guanin, 367  
 Guaranin, 369  
 Gumelastic, 276  
 Gumlac, 274  
 Gums, 441  
 Gummi-gutta, 275  
 Gun-cotton, 438  
 Gutta-percha, 276

## H

Hæmatoidin, 458  
 Hæmaphœin, 457  
 Hæmatoxylin, 421  
 Hæmatin, 421, 457  
 Hæmatein, 422  
 Halogens, 33  
 Harmalin, hydrocyanide of, 384  
 — 383

Harmin, 383  
 Hartite, 236  
 Hatschetin, 129  
 Helecoïdin, 427  
 Helenium camphor, 266  
 Helenin, 266  
 Helicin, 427  
 Heveen, 276  
 Hexachlorvaleryl, 152  
 Horn-tissues, 455  
 Humin, 459, 461  
 — substances, 459, 460  
 Hydrindin, 415  
 Hydroamyl, 112  
 Hydrocyamin, 373  
 Hydrocobaltcyanic acid, 322  
 Hydrocumid, 237  
 Hydrocymid, 237  
 Hydrocinnamid, 230



Hydrochrysid, 234  
 Hydrochrysamid, 254  
 Hydroanthracid, 233  
 Hydronaphthalid, 231  
 Hydrobenzid, 221  
 Hydrobenzamid, 227  
 Hydrotolid, 236  
 Hydrochinon, colorless, 194  
 ——— green, 195  
 ——— hydrochlorate of, 195  
 ——— rhomboidal, sulpho-hydrate  
     of, 195  
 Hydrocarbyls, 92  
 Hydroisocarbyls, 92  
 Hydromethyl, 95  
 Hydroethyl, 100  
 Hydroformyl, 125  
 Hydroacetyl-formyl, bromide of, 128  
 Hydroenanthyl, 154  
 Hydroazocarbyls, 334  
 Hydropolycarbyls, 168  
 Hydrindin, 415  
 Hydryls, 354  
 Hyoscyamin, 373

I

Idrialin, 235  
 Idryl, 234  
 Imasatin, 415  
 Imasetin, 415  
 Imabenzil, 225  
 Imperatoria oil, 264  
 India-rubber, 276  
 India-yellow, 422  
 Indigo-blue, 412  
 ——— brown, 412  
 ——— red, 412  
 ——— white, 414  
 ——— carmine, 414  
 ——— 411  
 Indin, 415  
 Indigin, 414  
 Inosit, 444  
 Inulin, 441  
 Iodal, 142  
 Iodethyl, 110  
 Iodamyl, 114  
 Iodacetyl, 141  
 ——— oxyhydrate of, 142  
 Iodanilin, 362  
 Iodmesityl, 146  
 Iodoform, 120  
 Iren, 266  
 Iron, acetate of, 134  
 ——— angelicate of, 173  
 ——— ferrocyanide of, 318  
 ——— hydrocyanate of, 319  
 ——— salicylite of, 208  
 ——— benzoate of, 245  
 ——— lactate of, 144  
 ——— protocyanide of, 316  
 ——— sesquicyanide of, 316  
 ——— sesquisulpho cyanide of, 326  
 ——— succinate of peroxide of, 179  
 Iron-potassa, tartrate of protoxide of, 291  
 Isatin, 414  
 Isatyd, 414

Isatimid, 415  
 Isatilin, 415  
 Isaten, 415

J

Jamaicin, 385  
 Jervin, 378  
 Juice-green, 424  
 Juniper-berry oil, 264

## K

Kakothelin, 380  
 Kakodyl, 386  
 ——— fluoride of, 389  
 ——— bichloride of, 388  
 ——— iodide of, 389  
 ——— nitrate of, 386  
 ——— oxychloride of, 388  
 ——— oxyiodide of, 389  
 ——— protobromide of, 389  
 ——— sulphokakodylate of sulphide of,  
     387  
 ——— sulphide of, 387  
 ——— oxide of, 386  
 ——— protochloride of, 387  
 ——— terchloride of, 388  
 ——— superchloride of, 388  
 ——— terbromide of, 389  
 Kapnomar, 201  
 Kreatin, 349  
 Kreatinin, 350  
 Kino tannin, 350  
 Kyanol, 358  
 Krystallin, 358

## L

Lactamid, 144  
 Lactates, 144  
 Lactid, 144  
 Lactin, 442  
 Lactyl, 143  
 Ladanum, 275  
 Laurostearyl, 157  
 Laurel-oil, 261  
 Laurns-camphor, 261  
 Lavender-oil, 263  
 Lead, bisulphocyanide of, 327  
 ——— acetates of, 134  
 ——— amid-camphorate of, 181  
 ——— anisylate of, 217  
 ——— butyrate of, 149  
 ——— elaidinate of, 176  
 ——— formate of, 120  
 ——— margarate of, 159  
 ——— nitrosalicylate of, 210  
 ——— pikrin-nitrate of, 203  
 ——— salicylite of, 209  
 ——— salicylamidate of, 211  
 ——— stearate of, 161  
 ——— succinate of, 179  
 ——— valerianates of, 152  
 ——— zinc-cyanide of, 322  
 ——— sugar of, 134  
 ——— cyanide of, 316  
 ——— malate of, 314  
 ——— sulphocyanide of, 326  
 ——— ferro-cyanide of, 318  
 ——— vinegar of, 134

Lead-plaster, 191  
 Leaf-wax, 167  
 — red, 418  
 — yellow, 418  
 Leather, 454  
 Lecanora ether, 407  
 Legumin, 451  
 Lemon-oil, 263  
 — camphor, 263  
 Leucin, 346, 348  
 Luteolin, 423  
 Lichenin, 441  
 Licorice sugar, 433  
 Lignin, 438  
 Lime, acetate of, 134  
 — angelicate of, 173  
 — butyrate of, 149  
 — chelidonate of, 300  
 — chlorphenisate of, 201  
 — citrate of, 298  
 — kinate of, 303  
 — lipinate of, 180  
 — malamate of, 289  
 — margarinate of, 159  
 — meconate of, 302  
 — œnanthate, 154  
 — oxalate of, 278, 282  
 — succinate of, 178  
 — tartrate of, 291  
 Limonin, 431  
 Liquor anodynus Hoffmanni, 103  
 Litmus, 408  
 Lophin, 227, 365

## M

Madder-root, 418  
 Manesia, mercurycyanide of, 322  
 Magnesia, sylvate of, 271  
 Malamid, 289  
 Malates, 288  
 Manganese, benzoate of protoxide, 245  
 — cyanide of, 316  
 Manna sugar, 431  
 Mannit, 432  
 Margarates, 159  
 Margarin, 187  
 Margaron, 162  
 Margaryl, 158  
 Marjorana camphor, 266  
 Mastich, 273  
 Meconin, 431  
 Meconates, 301  
 Medullin, 438  
 Melam, 368  
 Melamin, 368  
 Melanilin, 361  
 Melanoximid, 361  
 Melen, 129  
 Melissin, 116, 163  
 Melissinyl, 163  
 Melissyl, 116  
 — palmitate, 116  
 Mellan, 332  
 Mellan-lead, 332  
 Mellan-potassium, 332  
 Mellan-silver, 332  
 Mellitates, 306

Mellon, 332  
 Menispermin, 385  
 Menthén, 265  
 Mercaptan, 110  
 Mercury-allyl, 119  
 — sulphethyl, 110  
 — cyanides of, 316, 322  
 — fulminating, 331  
 — fulminate of protiodide, 331  
 — acetate, 135  
 — platinumcyanide of, 323  
 Mesit, 164  
 Mesiten, 164  
 Mesitol, 237  
 Mesitylen, 237  
 Mesityl, oxide of, 146  
 Mesitylid, oxyhydrate of, 146  
 — aldehyd, 145  
 Mesityloxyd-chlorplatinum, 146  
 Metals, sulphocyanides of, 326, 327  
 Metacetyl-urea, 325  
 Metacetyl, 147  
 Metaceton, 148  
 Metacetonyl, oxyhydrate of, 147  
 Metacinnamein, 230  
 Metacinnamin, 230  
 Metapectin, 446  
 Metamylon, 129  
 Metaldehyd, 131  
 Metatoluidin, 363  
 Metastyrol, 230  
 Methylen, 125  
 Methyl-acetyl, 145  
 Methyl-urea, 367  
 Methyl-formyl, 125  
 — chlorides of, 126  
 Methyl-amin, 357  
 Mythyl-amin, phosphide of, 385  
 Methylal, 163  
 Methyl-ethylamin, 357  
 Methyl-biethylamin, 357  
 Methyl-amylamin, 357  
 Methylen-formyl, protiodide of, 126  
 Methyl-mercaptan, 99  
 Methyl, 95  
 — acetate of, 163  
 — anisylate of, 219  
 — bromide of, 100  
 — bisulphide of, 99  
 — biphosphide of, 385  
 — basic borate of, 97  
 — acid borate of, 97  
 — butyrate of, 164  
 — basic formate of, 163  
 — binitrosalicylate of, 219  
 — benzoate of, 232  
 — bibrom-anisylate of, 219  
 — caprate of, 161  
 — capronate of, 164  
 — chloranisylate, 219  
 — chlorformate of, 163  
 — chloracetate of, 164  
 — carbonate of, 97  
 — chloride of, 100  
 — cyanurenate of, 337  
 — cyanate of, 325  
 — citrate of, 298

- Methyl, diphosphate of, 365  
 ——— formate of, 163  
 ——— fluoride of, 100  
 ——— iodide of, 99  
 ——— margarate of, 164  
 ——— mucate of, 299  
 ——— nitrate of, 97  
 ——— oxyhydrate of, 96  
 ——— oxalate of, 283  
 ——— oxamate of, 283  
 ——— oxide of, 96  
 ——— protosulphide of, 99  
 ——— succinate of, 184  
 ——— suberate of, 184  
 ——— salicylate, 218  
 ——— sulphocarbonate of, 97  
 ——— sulphate of, 98  
 ——— sulphocarbonate of sulphide of, 99  
 ——— trimtro-salicylate of, 219  
 ——— triphosphide of, 385  
 ——— sulphocyanide of, 327  
 ——— tersulphide of, 99  
 ——— valerianate of, 164  
 Milk-sugar, 442  
 Molybdenum, ferrocyanide of, 319  
 Morin, 401  
 Morphin, acetate of, 374  
 ——— hydrochlorate of, 374  
 Morphin, 374  
 Morphia, 374  
 Morphetin, 374  
 Moringyl, 173  
 Monarda oil, 266  
 ——— camphor, 266  
 Murexan, 343  
 Murexoin, 343-344  
 Musk, artificial, 264  
 Murexyd, 344  
 Myristicyl, 157  
 Myrosin, 451  
 Myricin, 166  
 Myrrh, 275
- N
- Naphtyl, 241  
 ——— chloride of, 241  
 ——— hydrochlorate of proto- and ter-  
 chloride of, 241  
 Naphtylchlorid-chlornaphtalid, 243  
 Naphtyl-naphtalid, chloride of, 241  
 Naphtyl-bichlornaphtyl, terchloride of, 242  
 Naphtyl-nitrid, 242  
 Naphtyl-nitrid-nitronaphtalid, 242  
 Naphtalidin-carbamid, 362  
 Naphtalid, 231  
 ——— oxide of, 232  
 ——— chloride of, 232  
 ——— hydrochlorate of chloride of, 232  
 ——— hydrobromate of bromide of, 232  
 Naphtalin, 231  
 Naphtalidin, 231, 362  
 Narcein, 375  
 Narcotin, 375  
 Narcotina, 375  
 Narcogenin, 376  
 Nacid Group, 192  
 ——— chloride of, 192
- Niceyl, 192  
 ——— Group, 192  
 Nicotin, 364  
 Nickel, cyanide of, 316  
 Nicotianin, 267  
 Nitranilin, 361  
 Nitracol, 154, 279  
 Nitroacetyl, 136  
 Nitrocapronyl, 153  
 Nitrochloracetyl, 141  
 Nitrometacetyl, 147  
 Nitromesidin, 363  
 Nitrocumidin, 363  
 Nitroparanicin, 363  
 Nitroharmalin, 384  
 Nitromannit, 433  
 Nitropropionyl, 147  
 Nitrophenetol, 206  
 Nitrocellulose, 438  
 Nitroferrocyanogen, 321  
 Nitroferri cyanides, 321  
 Nitrosynapyl-resin, 327  
 Nitrovaleryl, 152  
 Nitroanilin-urea, 367  
 Nitrobenzoyl, 246  
 ——— bioxychloride of, 247  
 Nitrogen bases, 355  
 ——— simple, 355  
 ——— paired, 365  
 Nitrobenzamid, 247  
 Nitrocumid, 237  
 Nitrogentianin, 424  
 Nitro-amyllum, 440  
 Nitro-furfurol, 194  
 Nitroanisol, nitro-anise oil, 205  
 Nitroanisid, 206  
 Nitrobenzid, 222, 223  
 Nitroazobenzid, 222  
 Nitropicramyl, 225, 227  
 Nitro-thionessal, 226  
 Nitro-cyanamyl, 229  
 Nitro-cinnamin, 231  
 Nitro-metacinnamin, 230  
 Nitro-cinnamid, 231  
 Nitro-naphtalid, 232  
 Nitro-tolid, 236  
 Nitro-mesidin, 238  
 Non-nitrogenous combinations, 433  
 Nitrotyrosin, nitrate of, 349  
 Nitrobutyryl, 149
- O
- Odmyl, 171  
 Odorin, 358  
 Oenanthe-ether, 165  
 Oenanthol, 154  
 Oenanthyl, 154  
 ——— oxyhydrate of, 154  
 Oil, anise, 205  
 ——— artificial formic, 193  
 ——— athamanta oreosilicium, 264  
 ——— birch, 264  
 ——— amber, 264  
 ——— cajeput, 261  
 ——— dracunculus, 207  
 ——— clove, 264  
 ——— cubeba, 264

- Oil, cascarilla, 264  
 — cedar, 265  
 — elemi, 263  
 — galanga, 264  
 — imperatoria, 264  
 — juniper-berry, 264  
 — laurel-berry, 264  
 — lavender, 264  
 — monarda, 266  
 — nutmeg-flower, 266  
 — origanum vulgare, 264  
 — peppermint, 265  
 — of wine, heavy, 128  
 — — light, 265  
 — apple, 268  
 — rue, 156  
 — copaiva, 263  
 — garlic, 168  
 — asafoetida, 171  
 — etheric mustard, 327  
 — mentha-viridis, 264  
 — laurel, 261  
 — olibanum, 203, 263, 273  
 — orange, 263  
 — — blossom, 263  
 — ferment, 263  
 — ocotea, 263  
 — petersilien, 264  
 — pepper, 264  
 — rose, 266  
 — rosemary, 266  
 — sabine-tree, 264  
 — spikenard, 264  
 — sage, 265  
 — sulphurise, 206  
 — thuja, 265  
 — valerian, 261  
 — wormwood, 263  
 — wormseed, 265  
 — wine, 265  
 Oleen, 129  
 Olefiant gas, 125  
 Olein, 187  
 Oleyl, 172, 174  
 — group, 172  
 Olivil, 427  
 Olivin, 427  
 Olibanum, 273  
 — oil, 263  
 Olyl, 174  
 Opian, 375  
 Opiammon, 305  
 Opianates, 305  
 Opoponax, 273  
 Organic vegetable bases, 372  
 Orcin, 408  
 Orcein, 408  
 Orchill, 408  
 Orellin, 423  
 Oresolon, 429  
 Orseille, 408  
 Oxalates, 282  
 Oxaluranilid, 360  
 Oxamethylan, 283  
 Oxamethan, 283  
 Oxamylan, 283  
 Oxanid, 282  
 Oxanilid, 359  
 Oxanilamid, 359  
 Oxatyl, 281  
 Oxide, cystic, 349  
 Oxypeucedanin, 424  
 Oxyprotein, 450  
 Oxyd, xanthic, 346  
 —, uric, 346  
 Ozokerite, 129
- P
- Palladium-allyl, 170  
 Palmitin, 187  
 Palmin, 188  
 Paraban, 330  
 Parakakodyloxyd, 389  
 Paranicin, 363  
 Paraffin, 129  
 Paramylen, 129  
 Paramylum, 440  
 Parapectin, 446  
 Parasalicyl, 214  
 Paraspiroyl, 214  
 Paramid, 307  
 Paracyan, 312  
 Papaverin, 376  
 Parietin, 410  
 Parilline, 431  
 Pectin, 445  
 — -substances, 444  
 — -ferment, 445  
 Pectose, 445  
 Pectase, 445  
 Pelosin, 383  
 Pereirin, 384  
 Persio, 408  
 Peruvian, 230  
 Peru-balsam, resin of, 272  
 Petenin, 357  
 Petersilien camphor, 264  
 Petrolen, 264  
 Peucedanin, 429  
 Phanoretin, 410  
 Phenol, 189, 199  
 — -potassa, 199  
 — -baryta, 199  
 Phenetol, 206  
 Phloretin, 426  
 Phloridzin, 425, 441  
 Phloridzein, 426  
 — -ammonia, 426  
 Phoron, 181  
 Phosbimethyl, 385  
 Phosmethyl-amin, 385  
 Phostrimethyl, 385  
 Phosphor bases, 385  
 Phosphorus, bioxychloride of, 218  
 Phtuanilid, 359  
 Phtalimid, 183  
 Phylloretin, 336  
 Picamar, 201  
 Picolin, 358  
 Picramyl, 287  
 — protobromide of, 227  
 — chloride of, 225  
 — proto-chloride of, 226  
 — oxide of, 224



- Pieramyl, sulphide of, 225-226  
 Picrotoxin, 431  
 Pigmentum nigrum oculi, 458  
 Pikroerythrin, 407  
 Pikryl, 225  
 Pimaron, 271  
 Piperin, 384  
 Pitoyin, 384  
 Pittakal, 201  
 Plasters, 189, 191  
 Platinum-allyl, 170  
     — bases, 394  
     — bichyanide of, 316, 322  
 Plumbagin, 424  
 Polychrom, 430  
 Potassium-cobalt, cyanide of, 322  
     — cyanide of, 315  
     — chlorocyanide of, 322  
     — nickelcyanide of, 322  
     — hydrocobaltcyanide of, 322  
     — zinccyanide of, 322  
     — mercurycyanide of, 322  
     — silbercyanide of, 322  
     — platinumcyanide of, 323  
     — platincyanide of, 323  
     — aurocyanide of, 323  
     — sulphocyanide of, 326  
     — urate of, 340  
     — glyccoll-sulphate of, 347  
         — -nitrate, 347  
 Potassa, acetate of, 133  
     — allophanate of, 337  
     — amyloxyd-sulphocarbonate, 114  
     — anacardate of, 278  
     — anisylate of, 217  
     — benzoate of, 245  
     — bibromsalicylate of, 213  
     — bichlorsalicylate of, 213  
     — binitrosalicylate of, 213  
     — camphorate of, 182  
     — chelidonate of, 301  
     — chloracetate of, 139  
     — chloranilate of, 197  
     — cholalate of, 278  
     — citraconate of, 295  
     — citrates of, 298  
     — cyanate of, 323-324  
     — cyanurenate of, 327  
     — cyanurate, 337  
     — ethalate of, 153  
     — elaidate of, 174  
     — fumarate of, 286  
     — glaucomelinate of, 403  
     — glyccoll-nitrate of, 348  
     — glyccoll-sulphate of, 347  
     — hippurate of, 250  
     — inosinate of, 350  
     — isatiniate of, 415  
     — itaconate, 295  
     — kinate of, 303  
     — lactate of, 111  
     — malate of, 188  
     — malamine, 385  
     — margarate, 159  
     — meconate of, 301  
     — mellitate, 306  
     — methyloxyd-tartrate of, 292  
     — Potassa, methyl-salicylate of, 219  
         — myristicate of, 157  
         — mucate of, 299  
         — narcotate of, 376  
         — nitracolate of, 279  
         — olidate of, 158  
         — œnanthate of, 154  
         — oxalate of, 282  
         — propionate of, 147  
         — purpate of, 343  
         — rhodizonate of, 308  
         — rubrin-nitrate of, 203  
         — silver-fulminate of, 331  
         — silvate of, 279  
         — salicyl-amidate of, 212  
         — salicylite of, 208  
         — salicylate of, 208  
         — sesquichelidonate of, 300  
         — sesquicarbonate of, 298  
         — saccharate of, 298  
         — stearinate of, 298  
         — succinate, 178  
         — sulphacetate, 142, 178  
         — tartrate of, 290  
         — urate of, 340  
         — valerianate of, 151, 290  
         — zinc-fulminate of, 151, 290  
 Potassium-manganese, cyanide of, 317  
     — -barium, ferrocyanide of, 318  
     — -iron, ferrocyanide, 318  
     — ferrocyanide of, 317  
     — ferricyanide of, 319  
     — chromocyanide of, 322  
     — aurocyanide of, 323  
     — auricyanide of, 323  
     — mangancyanide of, 322  
     — -manganese, ferrocyanide of, 318  
     — nickelcyanide of, 322  
     — -zinc, ferrocyanide of, 318  
 Potash, oxalate of, 282  
 Potassa-soda, 298  
     — sesquicarbonate of, 298  
 Potassa-arsenious-acid, tartrate of, 292  
     — bitartrate of, 292  
 Potassa-boracic-acid, tartrate of, 291  
 Potassa-ammonia, tartrate of, 291  
 Potassa soap, 189  
 Propion, 148, 186  
 Propionates, 147  
 Propionamid, 147  
 Propionyl, 147  
     — oxyhydrate of, 147  
 Propyl, 112  
 Propyl-formyl, 128  
 Propylamin, 357  
 Propylen, 128  
     — bromide of, 128  
     — chloride of, 128  
 Protein, 448  
     — substances, 447  
     — combinations, 448  
 Pseudomorphin, 375  
 Pseudoerythrin, 407  
 Pseudo-ornin, 408  
 Pulsatillen-camphor, 267  
 Purpurin, 419  
 Purree, 422

Purrenon, 423  
 Pyren, 234  
 Pyrocatechin, 403  
 Pyroxylin, 434

## Q

Quadrichlorbutyryl, 150  
 Quadrichlorbutyryl, oxyhydrate of, 150  
 Quadrichlorbutyral, 150  
 Quadrichloronaphthalin, 242  
 Quadrichloroentanhyll, 155  
 Quadrichlorvaleryl, 152  
 Quassia, 431  
 Quercitrin, 402  
 Quercitron-tannin, 398  
 Quinin, 382  
 ——— sulphate of, 382  
 ——— hydrochlorate of, 382  
 ——— amorphous, 383  
 Quinia, 382

## R

Resinein, 271  
 Resineon, 271  
 Resinon, 271  
 Resins, 268  
 Retinol, 235  
 Retinite, 235  
 Retinyl, 235, 237  
 Retinaphtha, 236  
 Retisterin, 235  
 Rhodan-metals, 326  
 Ricinates, 176  
 Rose-camphor, 266  
 Roccin, 408  
 Roccein, 408  
 Roccinin, 407  
 Roccelin, 407  
 Roccellinin, 407  
 Rocceglucin, 408  
 Rubiacin, 419  
 Rubrin, 419  
 Rufin, 216, 427  
 Rutilin, 216, 427

## S

Sabadillin, 378  
 Saccharates, 299  
 Sagapenum, 275  
 Salicyl, 207  
 Salicin, 215, 426  
 Saligenin, 215  
 Saliretin, 215, 427  
 Salicon, 199  
 Salicyl-nitrid, 205, 212  
 Salicylates, 208  
 Salicylimid-amid, 208  
 Salicylimid-iron, 208  
 Salt-bases, organic, 346  
 ——— volatile, 355  
 ——— non-volatile, 355  
 ——— paired, 355  
 Sandarach, 272  
 Santalid, 422  
 Santaloid, 422  
 Santalidid, 422  
 Santaloidid, 422

Santonin, 431  
 Santalin, 422  
 Saponin, 432  
 Sarkosin, 346  
 Sassaparil, 431  
 Sassafras camphor, 266  
 Scammonium, 375  
 Scheererite, 236  
 Selenaldin, 371  
 Selen-ethyl, 110  
 Seminaphthalidin, 362  
 Senegin, 431  
 Silver, 135  
 ——— acetate of, 135  
 ——— anisylate of, 217  
 ——— acrate of, 143  
 ——— benzoate of, 245  
 ——— camphorate of, 182  
 ——— cyanide of, 316  
 ——— chloracetate of, 139  
 ——— chlorniceinate of, 193  
 ——— chlorsuccinate of, 145  
 ——— cholesterinate of, 280  
 ——— cyanate of, 324  
 ——— cyanurate of, 337  
 ——— euchronate of, 307  
 ——— fulminating, 330  
 ——— kinate of, 303  
 ——— mellitate of, 306  
 ——— oenanthate of, 154  
 ——— oxalate of, 282  
 ——— phthalinate of, 183  
 ——— propionate of, 147  
 ——— silver-fulminate of, 330  
 ——— salicylamidate of, 212  
 ——— sulphamyl-sulphate of, 114  
 ——— sulphacetate of, 142  
 ——— sulphocyanide, 327  
 ——— valerianate, 152  
 Silver-allyl, nitrate of, 169  
 Silver, cyanurate of, 337  
 Silver-sulphethyl, 110  
 Sinapolin, 327, 371  
 Sinapin, 429  
 Synammin, 370  
 Smilacin, 431  
 Soaps, 189  
 Soda soap, 190  
 Soda, urate of, 340  
 ——— acrylate of, 143  
 ——— anisylate of, 217  
 ——— benzoate of, 245  
 ——— formate of, 120  
 ——— chelidonate of, 301  
 ——— kinate of, 303  
 ——— cholate of, 351  
 ——— citrate of, 298  
 ——— croconate of, 308  
 ——— acetate of, 134  
 ——— inosinate of, 350  
 ——— mucate of, 299  
 ——— laurostearate of, 157  
 ——— malaminatate of, 289  
 ——— margarate of, 160  
 ——— pikranate of, 205  
 ——— urate of, 340  
 ——— stearate of, 161

- Soda, stearophanate of, 162  
 ——— tartrate of, 291  
 ——— sesquicitrate of, 298  
 ——— protochelidonate of, 300  
 ——— bichelidonate of, 301  
 ——— bitartrate of, 291  
 Sodium, mercury-cyanide of, 322  
 ——— cyanide of, 316  
 ——— nickel-cyanide of, 322  
 ——— ferrocyanide of, 318  
 Soda-potassa, tartrate of, 291  
 Solanin, 377  
 Spaniolitmin, 409  
 Spermaceti, 166  
 Spiritus nitri dulcis, 106  
 Spikenard oil, 264  
 Spirol (*vide* Phenol), 199  
 Spiroyl (*vide* Salicyl), 207  
 Spiroylimid, 208  
 Spiroylbromid, 212  
 Starch, 439  
 Starch-sugar, 444  
 Starch-meal, 444  
 Stearin, 187  
 Stearates, 160  
 Stearophanyl, 162  
 Stearophanin, 187  
 Stibethyl, 391  
 ——— oxide of, 392  
 ——— chloride of, 393  
 ——— bromide of, 393  
 ——— sulphate of, 392  
 ——— nitrate of, 392  
 ——— sulphide of, 392  
 ——— iodide of, 392  
 Stibamyl, 393  
 Stibethylium, 393  
 Stibmethyl, 391  
 Stibmethylum, 391  
 ——— oxide of, 391  
 ——— sulphate of, 391  
 ——— bicarbonate of, 391  
 ——— iodide of, 391  
 ——— chloride of, 391  
 Stibmethylethylum, 391  
 Stilben, 223  
 Stilbyl, protochloride of, 227  
 Stiracin, 229  
 Strontia, lipinate of, 180  
 Struthiin, 431  
 Strychnin, 378  
 ——— hydrochlorate of, 380  
 ——— hydriodate of, 380  
 ——— nitrate of, 380  
 ——— sulphate of, 379  
 Strychnia, 378  
 Styracon, 230  
 Styron, 229  
 Suberanilid, 359  
 Succinates, 178  
 Succinalid, 359  
 Succinanilid, 359  
 Succyl-group, 176  
 Succisterin, 236  
 Sugar, common or cane, 443  
 ——— fruit, 443  
 ——— milk, 442  
 Sugar, grape, 444  
 Sulpho-amyl, 114  
 Sulpho-furfurol, 194  
 Sulpho-hydrochinon, brown, 195  
 Sulpho-hydrochinon, yellow, 195  
 Sulphohydrobenzoyl, 227  
 Sulphobenzid, 222, 223  
 Sulphanisol, 206  
 Sulph-isatin, 415  
 Sulph-isatyd, 415  
 Sulphonaphthalid, 232  
 Sulphonaphthalin, 232  
 Sulphotolid, 237  
 Sulphacetyl, 142  
 Sulphethyl-sulphocarbonate, 109  
 Sulphoform, 120  
 Sulphometaldehyd, 131  
 Sulpho-gold-sulph-allyl, 170  
 Sulpho-methylan, 98  
 Sulpho-palladium-sulph-allyl, 170  
 Sulpho-mercury-sulph-allyl, 170  
 Sulpho-platinum-sulph-allyl, 170  
 Sulpho-silver-sulph-allyl, 170  
 Sulphomesityl, 146  
 Sulphur-allyl, 169  
 Sulphochlor-platinum-allyl, 170  
 ——— mercury-allyl, 170  
 Sulpho-hydroodmyl, 171  
 Sulphoferulyl, 171  
 Sulphocarbonilid, 360  
 Sulphisatyd, 415  
 Sulphocyanides, 326, 327  
 Sulphomellan-metals, 333  
 Sulphomellan, 333  
 Sugar, different species of, 442  
 Surinamin, 385  
 Synaptase, 451

## T

- Tannin, 395  
 ——— catechu, 397  
 ——— coffee, 397  
 ——— morus, 397  
 ——— kino, 399  
 ——— cinchona, 399  
 ——— china, 399  
 ——— gallnut, 398  
 ——— bohea, 400  
 ——— quercitron, 398  
 Tartarus ammoniatus, 291  
 ——— boraxatus, 291  
 ——— martialis, 291  
 ——— tartarisatus, 291  
 Tartar emetic, 292  
 Taurin, 349  
 Tartrates, 290  
 Tekoretin, 236  
 Tellurethyl, 110  
 Telluraldin, 371  
 Telerythrin, 407  
 Terecryl, 173  
 Tereben, 259  
 Terebilen, 259  
 Terebenes, 256  
 Terebencyl, 192  
 Terpin, 259  
 Terpinol, 259

Tetrachlorchinon, 197  
 Tetrachlornaphtalin, 241  
 Thebain, 375  
 Thein, 369  
 Theobromin, 369  
 ———— nitrate of, 369  
 ———— hydrochlorate of, 369  
 Thialdin, 371  
 ———— hydrochlorate of, 371  
 Thialole, 109  
 Thiosinnamin, 327, 369  
 Thionessal, 226  
 Tobacco-camphor, 267  
 Tolen, 239  
 Tolin, 236  
 Tolid, 236  
 ———— chloride of, 236  
 Toluidin, 336, 362  
 Toluol, 236  
 Toluyl, 251  
 Tournesol, 409  
 Tribromanilin, 362  
 Tribromcumidin, 363  
 Tribromtoluidin, 363  
 Trichloranilin, 362  
 Tribromanisol, 212  
 Trichlorchinon, 196  
 Trichlorhydrochinon, 196  
 Trichlornaphtalin, 241  
 Triethyl-amin, 357  
 Trinitranisol, 212  
 Trinitro-mesitol, 237  
 Trinitronaphtalid, 242  
 Trinitrobenzin, 241  
 Trioxypotein, 453  
 Turpentine, oil of, 258  
 ———— hydrobromate of oil of, 259  
 ———— hydrochlorate of oil of, 259  
 ———— hydriodate of oil of, 259  
 ———— varnish, 270  
 Tyrosin, 349

## U

Ulmin, 459, 460  
 Ulmin-substances, 460, 461  
 Uramil, 342  
 Urates, 339  
 Urea, 324, 325, 335, 367  
 ———— nitrate of, 367  
 ———— oxalate of, 367  
 Urenoxyd-ammonia, 336  
 Uren, 334  
 ———— oxide of, 334  
 Uric-oxyd, 346  
 Urethylan, 99

## V

Valeryl, 150  
 ———— oxyhydrate of, 150  
 ———— acetate of oxychloride of, 152

Valeral, 150  
 Valeramid, 150  
 Valer-aldehyd, 150  
 Valerianates, 150  
 Valeron, 153  
 Valero-nitryl, 152  
 Valeren, 129  
 Valerol, 265  
 Valyl, 111  
 ———— valerianate of, 111  
 Valylen, 111, 128  
 ———— chloride of, 111, 128  
 Vegetable matters, indifferent, colorless, 425  
 Veratrin, 178  
 Veratria, 178  
 Verdigris, 134  
 Viscin, 277  
 Vitellin, 454  
 Violet camphor, 266

## W

Wax, Chinese, 166  
 ———— cork, 167  
 ———— white, 167  
 ———— palm, 167  
 ———— leaf, 167  
 ———— myrica, 167  
 ———— cerenauba, 167  
 ———— ocuba, 167  
 ———— butter, 167  
 Wine oil, 265  
 Wood-fibrin, 438  
 Wood-spirit, 96  
 Wood-ether, 96  
 Wood-vinegar, 132  
 Wormseed oil, 265  
 Wormwood oil, 263

## X

Xanthine, 346  
 Xanthic-oxyd, 346  
 Xanthogen-amid, 108  
 Xanthorhamnin, 224  
 Xanthorhæa hastilis, resin of, 275  
 Xanthophyl, 418  
 Xylidin, 363  
 Xylit, 164  
 Xylit-naphtha, 164  
 Xyloid, 237  
 Xyloidin, 237, 440  
 Xyloidine, 438

## Z

Zinc, acetate, 134  
 ———— cyanide of, 316  
 ———— lactate of, 144  
 ———— sulphocyanide of, 326  
 ———— valerianate, 152  
 ———— zinc-sulminate, 331



# ERRATA.

- Page 49, " 8 from bottom, *for* "common charcoal" *read* caking coal.  
 " 96, " 4, *for* "Ethyl" *read* Methyl.  
 " 99, " 37, *for* "(MS)" *read* (MeS).  
 " 105, line 7, *for* " $\text{BO}_3$ " *read*  $\text{BoO}_3$ .  
 " 105, " 43, *for* "PO" *read*  $\text{PO}_5$ .  
 " 106, " 9, *for* "Nitrate" *read* Nitrite.  
 " 107, " 2, *for* "hydrosulphate of ethyl" *read* hydrosulphethyl.  
 " 108, " 7, *for* "Hanthogenamid" *read* Xanthogenamid.  
 " 113, " 36, *for* "Nitrate" *read* Nitrite.  
 " 136, " 31, *for* "Acetyl-Platinchloride, Plantinchloride" *read* Acetylplatin-  
 chloride-platinchloride.  
 " 146, " 1, at bottom, *for* "acephoric" *read* acephosic.  
 " 192, " 23, *for* "Paranicin" *read* Paranicen.  
 " 192, " 27, *for* "Hence paranicin" *read* Hence paranicen.  
 " 264, " 25, *for* "bitula" *read* Betula.  
 " 266, " 11, *for* "Oil" *read* Camphor.  
 " 415, " 1, at top, *for* "imasitin" *read* imasatin.

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| " 2. <i>The Dignity of the Art and its Relations to Science.</i>  | CHAP. 17. <i>The Constituents of Fats, their Properties and Composition:</i> Stearine, Stearic Acid and Salts; Margarine, Margarinic Acid and Salts; Olein, Oleic Acid and Salts; Cetine, Cetyllic Acid; Phocanine, Phocenic Acid and Salts; Butyrine, Butyric Acid and Salts; Caproic, Capric Acid; Hircine, Hircic Acid; Cholesterine. |
| " 3. <i>Affinity and Chemical Equivalents:—Explanation of.</i>  | " 18. <i>Basic Constituents of Fats:—</i> Glycerin, Ethal.   |
| " 4. <i>Alkalies.</i> —Lime, Potassa, Soda, Ammonia.  | " 19. <i>Theory of Saponification.</i>   |
| " 5. <i>Alkalimetry.</i>  | " 20. <i>Utensils:—</i> Steam Series, Bugadiers or Ley Vats, Soap Frames, Caldrons, &c.  |
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| " 7. <i>Origin and Composition of Fatty Matters.</i>  | " 22. <i>Remarks.</i> —Preliminary to the Process for Making Soap.   |
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